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INVESTIGATION OF SURFACE FILMS - CHESAPEAKE BAY ENTRANCE

William G. MacIntyre, et al

Virginia Institute of Marine Science

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Indigenous surface films in the study area were analyzed for lipid and chlorinated hydrocarbon content. Hydrocarbons were 300-500 microgram per liter and fatty acids and esters 700-7800 microgram per liter in surface film samples. Chlorinated hydrocarbons were generally less than 100 parts per trillion in surface films, in contrast to some earlier high concentrations found in Biscayne Bay. Surface film analysis limitations imposed by sampling methods are discussed. Plankton in slick, non-slick, and subsurface water were counted. Populations were higher in surface than subsurface water, and higher in non-slick than in slicked surface water. (EPA)

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February 1974

INVESTIGATION OF SURFACE FILMS—CHESAPEAKE BAY ENTRANCE

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ABSTRACT

Experimental point source oil releases have been conducted in the Chesapeake Bay mouth area. Predictions of oil slick motion were tested, and slicks were sampled and analyzed to measure their aging rates over periods up to 32 hours. Remote sensing techniques were used to detect and measure the spreading rate of oil. Some laboratory oil film aging experiments were done to further document and elucidate aging processes. Results indicate a reasonable motion prediction, an explanation of the non-biological initial aging of oil films, and a fair corroboration of a theoretical oil spreading model.

Indigenous surface films in the study area were analyzed for lipid and chlorinated hydrocarbon content. Hydrocarbons were 300-500 μg/liter and fatty acids and esters 700-7800 μg/liter in surface film samples. Chlorinated hydrocarbons were generally less than 100 parts per trillion in surface films, in contrast to some earlier high concentrations found in Biscayne Bay. Surface film analysis limitations imposed by sampling methods are discussed. Plankton in slick, non-slick, and subsurface water were counted. Populations were higher in surface than subsurface water, and higher in non-slick than in slicked surface water.

This report was submitted by the Virginia Institute of Marine Science in fulfillment of Project Number 15080 EJ0 under the (partial) sponsorship of the Office of Research and Monitoring, Environmental Protection Agency. Work was completed as of March 17, 1972.

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CONCLUSIONS

A computer program has been developed to enable prediction of oil slick trajectories from available wind and tidal current information. The accuracy of prediction depends on tidal current data quality and knowledge of steady currents. Significant errors may occur in locations where current systems are poorly described.

The most important process in initial aging of fuel oils at sea is the loss of volatile compounds through evaporation. Loss of material by dissolution into seawater is quite small and little change is produced in the oils by this aging mechanism.

The components of a fuel oil slick which dissolve at greatest concentration into seawater under aerated, agitated conditions are naphthalene, and the several methyl-substituted naphthalenes.

Quantitative determination of the degree of aging of a fuel oil can be made from the boiling range composition of the original oil and gas chromatographic analysis of n-paraffins in original and aged oil samples.

Photography is useful for oil slick detection and discrimination. The near ultraviolet band is best for imaging edges and thin slicks. The green band best delineates thick oil regions. Color film is useful, as it distinguishes thick from thin oil, and fuel oil from recent lipid slicks.

No. 2 fuel oil is distinguished from No. 4 and 6 fuel oils by its lack of negative contrast in blue and green band photographs.

Oil slick spreading was found to fit a theoretical model for small volume spills of No. 2 and 4 fuel oils. No. 6 fuel oil did not spread in our tests.

In an estuarine environment the surface microlayer contains more phytoplankton than water at one meter depth, and species diversity is lower at the surface than at one meter. Phytoplankton population in the surface microlayer are lower in slick than non-slick areas. This result was obtained with both light fuel oil and natural lipid slicks. Samples were taken seasonally and show the usual temperate zone species pattern with peak populations in March and September.

Chlorinated hydrocarbons (CHP) and polychlorinated biphenyls (PCB) were detected in indigenous estuarine slicks and subsurface water. Total chlorinated hydrocarbon and CHP concentrations were generally higher in surface than subsurface water, while PCB concentration was similar in surface and subsurface water.

Lipid analysis of indigenous surface slicks from Chesapeake estuarine locations showed them to be predominantly fatty acids and esters of recent biological origin. The minor hydrocarbon amounts were petroleum products with the G.C. characteristics of a light fuel oil.

SECTION II

RECOMMENDATIONS

Detailed current studies should be conducted in probable spill areas to permit more accurate prediction of oil transport. The computer program given here should be used for oil spills where tidal currents are available, and slicks will not beach for at least 12 hours.

A quick-deployment air dropped current meter system should be developed for use at spill locations where prior information on steady and tidal currents is unavailable. This would make a rough prediction of slick motion possible.

The validity of the assumption of linear vector addition of steady current and wind velocity should be tested by experiment and theoretical analysis, so that conditions under which the predictive model fails may be understood with consequent improvement of the model.

Large scale turbulence produces unsteady non-tidal currents which are not included in the present prediction model. This phenomenon should be investigated, perhaps by remote sensing methods, for coastal regions.

Long term aging experiments on air-barrier confined slicks of crude and residual fuel oils should be designed to investigate tar ball formation. The aged synthetic tar balls should be compared with those collected in the Atlantic Ocean. This work would permit greater understanding of semi-permanent oil pollution in the world ocean.

Further oil component dissolution in seawater experiments should be conducted using GC-MS analysis. This work will recognize the non-equilibrium nature of release of oil aromatics and their partitioning between oil and water. The effect of oil dispersants in keeping otherwise volatile toxic oil aromatics in the water column should be investigated.

Photography should be used for daylight remote detection and discrimination of oil spills. An infrared scanner should be used for night oil spill detection. Photography of oils should be conducted with films and filters suggested in this report.

Further analysis of the oil spreading model verified here should be made and the viscosity of oil included in the model.

Toxicity of oil and oil components on phytoplankton should be a major concern, because there is prior evidence that oil adversely affects the primary aquatic producers. This work indicates some effects of organic films on surface phytoplankton populations.

Attempts to establish the importance of organic surface films in concentration and transport of chlorinated hydrocarbons should be discontinued until adequate separation methods for compound classes are developed, a means of sampling solely the organic surface layer without water is devised, and methods to determine the age and prior history of a slick are found. These requirements seem unsatisfiable in the near future.

Information on indigenous estuarine slick composition obtained in this study indicates the relatively unpolluted situation in the sampled region. This work should be repeated in other areas to establish the petroleum hydrocarbon content of our coastal surface waters.

SECTION III

INTRODUCTION

A series of experimental oil releases have been conducted in the Chesapeake Bay and Virginia coastal waters. Observations and conclusions from these and ancillary laboratory studies are presented in this report.

The several objectives of this program were:

1.) Description and prediction of the motion of point source oil spills under varying wind and tidal current conditions.

2.) Collection of oil from slicks at serial times after release, and analysis of these samples to determine the loss of water soluble and volatile constituents.

3.) Photographic and passive radiation imaging at serial times after oil release to establish oil spreading rates, document slick shape, and fix its orientation relative to measured winds and currents.

4.) Determination of water surface photoplankton population and species composition in film covered and film free areas.

5.) Chemical analysis of natural films collected in the Chesapeake Bay estuarine system to establish their content of petroleum compounds, chlorinated organics, and recently formed lipid substances.

Table 1 is a chronological listing of the experimental oil releases which yielded information relating to the first three objectives above. This tabulation should be referred to subsequently in this report, because oil releases are identified here by release date.

A map of the Virginia Maritime Area (Fig. 1) shows the approximate locations of the oil releases. Detailed navigational data are available on request from the reporting agency.

Oil sources were: No. 6 and No. 4 fuel oil from the Norfolk terminal of ESSO and originating from mixed residues and distillates of Nigerian and Venezuelan crude processed by the Lago Refinery, Aruba, N.W.I., No. 2 fuel oil from various local heating oil company distributors, and menhaden oil from Haynie Products Co., Reedsville, Virginia.

Table 1. Experimental Oil Releases

Date	Oil Type	Release Location	Kind of Observation	Volume Released (gal.)	Observation Period (hrs.)
Sept. 12, '69	6	Ches. Lt. Tower	B	100	
Sept. 25, '69	6/menhaden	Bridge Tunnel	A	5/30	5
Sept. 26, '69	6/menhaden	York River	B	5/10	-
Oct. 27, '69	6	Bridge Tunnel	B	25	6
Nov. 24, '69	6	Bridge Tunnel	A	25	4
Dec. 6, '69	6	Bridge Tunnel	A	25	7
Jan. 28, '70	6	Bridge Tunnel	A	6	7
Feb. 13, '70	6	Bridge Tunnel	A	5	5
Mar. 9, '70	2/6	Bridge Tunnel	A	50	7
May 6, '70	6	Bridge Tunnel	A	30	3
Aug. 12, '70	2	Ches. Lt. Tower	B	200	8
Sept. 14, '70	4	Ches. Lt. Tower	A	200	24
Nov. 6, '70	4	York River	A B C	150	9
Dec. 3, '70	6	Ches. Lt. Tower	B C	200	30
Jan. 21, '71	2	Ches. Lt. Tower	A B C	200	7

Table 1. (Cont'd). Experimental Oil Releases

Date	Oil Type	Release Location	Kind of Observation	Volume Released (gal.)	Observation Period (hrs.)
Jan. 22, '71	4	Ches. Lt. Tower	A C	200	9
Mar. 18, '71	2	York River	C	200	6
Apr. 26, '71	4	Ches. Lt. Tower	A B C	250	16
Jun. 23, '71	6	Mid Ches. Bay	C	65	31
Aug. 3, '71	4	Ches. Lt. Tower	A B C	200	32
Aug. 30, '71	2	Ches. Lt. Tower	A B C	200	10
Sept. 14, '71	6	Ches. Lt. Tower	A B C	200	25
Oct. 13, '71	2/6	Ocean Station	A B C	200/200	7/24

A = track B = Remote sensing C = Sampling

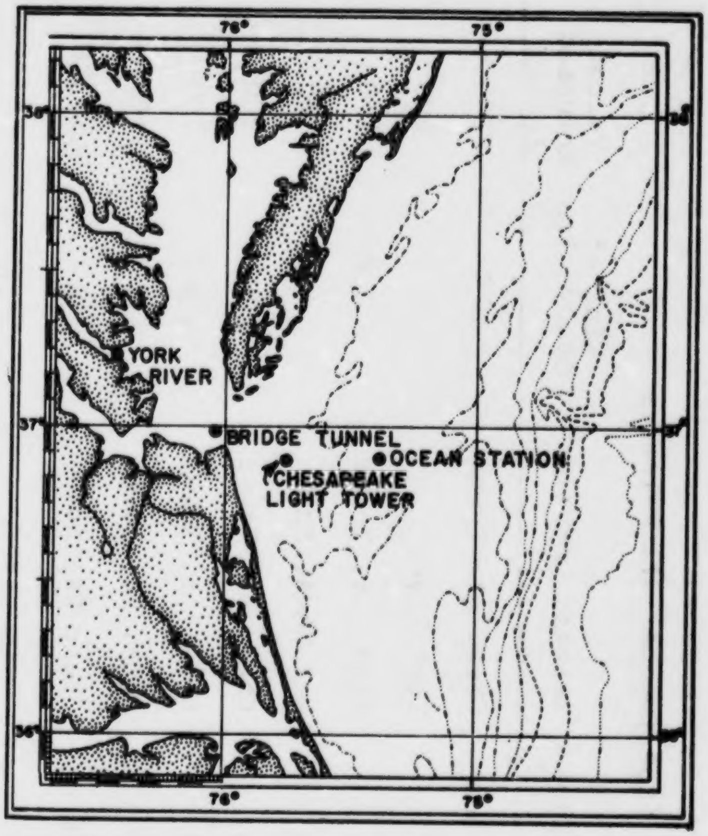
76°
75°
38°
38°
YORK
RIVER
37°
37°
BRIDGE TUNNEL
OCEAN STATION
CHESAPEAKE
LIGHT TOWER
36°
36°
76°
75°

Fig. 1. Oil release experiment locations.

Oil was obtained in separate batches for each release, and each batch had a potentially different history of well source, refining treatment, and aging in storage. Thus, chemical comparisons are made only within a set of oil release samples, but it was assumed that bulk physical properties of all batches of a particular type of fuel oil were similar.

Releases were made from storage tanks or barrels carried on board the vessel used to maintain station during observation of the oil slick. Vessels were provided by N.A.S.A., the U. S. Coast Guard, and the U. S. Navy. The N.A.S.A. ship "Range Recoverer" was most often used.

The release vessel served as a navigation and weather observation platform, a communication center for directing activities of remote sensing aricraft, and a mother ship for motorized inflatable boats used to sample the oil and gather remote sensing ground truth information.

Direct observation and sampling of oil slicks was not possible during hours of darkness, so flasher drogues that floated in or near the slicks were deployed in the evening and followed till morning. The slick could then, in some cases, be visually relocated and further studied.

A contingency plan, which stated action to be taken by agencies involved in this study in the event an experimental oil spill should endanger shorelines, was adopted. Notification was given to E.P.A., U.S.C.G., the U. S. Army Corps of Engineers, and the Virginia Water Control Board prior to each release. Weather-slick release point combinations were selected to minimize the possibility of beaching the oil. Oil slicks were always followed until no longer detectable or practical to sample, and, since there were no unfortunate incidents, the contingency plan was never applied.

Studies on the latter two of the stated program objectives, plankton population and chemical composition of occurring slicks of origin not related to the experimental oil release program, were conducted entirely in the Chesapeake Bay. The work was concentrated in the York River and Chesapeake Bay Bridge-Tunnel regions.

SECTION IV

OIL SLICK MOTION

Effective control and cleanup of oil slicks often requires predictions of oil slick motion. In marine areas, slick trajectories are the net result of tidal currents, wind generated currents, and motion due to local wind stress. To establish the relative importance of these factors, slug oil releases in this program were tracked throughout each experiment by the navigational equipment available on the oil release vessels. These releases are listed in Table 1.

A few field observations and theoretical treatments indicate that oil slicks move with the wind at 2.3 to 5 percent of the wind speed (Batelle, 1969, 1967; Kolpack, 1969; Smith, 1968). This percentage value has been termed a "wind factor." Wind generated surface currents have a similar wind factor (Laevastu, 1962; James, 1968; Doebler, 1966; Hela, 1952; Tolbert and Salsman, 1964), so a distinction must be made between the overall wind factor, and the relative wind factor. Slick position data can be used to calculate a total slick velocity $\vec{S}$. The wind vector $\vec{W}$ can be divided into $\vec{S}$ to give the overall wind factor. If the local surface current vector $\vec{C}$ is measured, the slick velocity data can be reduced by subtracting $\vec{C}$ from $\vec{S}$ to give $\vec{R}$, the component slick motion due to local wind stress. The value $|\vec{R}|/|\vec{W}| \times 100$ is referred to as the relative wind factor.

In the experiments conducted in Chesapeake Bay on the dates shown in Table 2, the relative wind factor was calculated. Overall wind factors were calculated for those other releases in which navigation data were available but surface currents were not measured.

Local surface currents, $\vec{C}$, were determined by tracking a current drogue from the observation vessel, which provided simultaneous position fixes. The dorgue had four vertical orthogonal 25 centimeter square vanes, and was weighted to place the vanes 1 meter below the water surface. A light bamboo pole carrying a diver's flag at 6 ft above the water surface made the drogue easily visible. The wind drag on the drogue was 0.25 percent, measured against surface water masses marked with Rhodamine WT with winds of 20 knots and white capped waves 0.3 to 0.7 meter high. Data were not corrected for this small wind factor.

Table 2. Oil Slick Motion and Relative Wind Factor.

Experiment Date and Vol. (gal.)	Water Temp. (°C.)	Time[1] (hours MT)	Relative Velocity (knots)	Wind Velocity (knots)	Relative Wind Factor (%)
BUNKER C FUEL OIL					
24 Nov. 69	10.0	1319-1440	0.163 NW	15 N	0.8 (45°Left)[2]
25		1440-1534	0.24 NNW	15 N	1.6 (10°Left)[2]
6 Dec.	6.6	1205-1320	0.4[3] NW	10 N	0.88 (50°Left)[2]
25		1345-1545	0.0	7 N	0.0
28 Jan. 70	0.5	1121-1325	0.02 ESE	8 ESE	0.25
6		1500-1545	0.02 ESE	8 ESE	0.25
13 Feb.[4]	3.0	1251-1604	0.0	3.5 NW	0.0
5					

---

[1] Portions of experiments containing most reliable quantitative data.

[2] Orientation of slick vector relative to wind vector.

[3] Velocity magnitude value exaggerated by extensive slick spreading and dispersion. Simultaneous measurements on two drogues formed the basis for reducing the value in calculating a wind factor

[4] 20 gallons of SAE 30 oil added to increase slick visibility.

Table 2. (Cont'd.). Oil Slick Motion and Relative Wind Factor.

Experiment Date and Vol. (gal.)	Water Temp. (°C.)	Time[1] (hours MT)	Relative Velocity (knots)	Wind Velocity (knots)	Relative Wind Factor (%)
BUNKER C FUEL OIL					
9 Mar.	2.2	111-1152	0.3 NE	17 NE	1.7
50[5]		1321-1404	0.25 SE	12 NNE	0.0 (112°Right)[2]
		1404-1417	0.0	12 N	0.0
6 May	15.0	1339-1408	0.184 NNW	19.5 NNW	0.95
30		1408-1448	0.185 NNW	18 NNW	1.03
		1448-1510	0.135 NNW	16 NNW	0.85
		1510-1533	0.257 NNW	14.5 N	1.75 (10°Right)[2]
NO. 2 FUEL OIL					
9 Mar.	2.2	1115-1517	0.0	14 NNE	0.0
50[5]					
MENHADEN FISH OIL					
25 Sept. 69	21.0	1006-1200	0.0	4 W	0.0
25		1200-1235	0.4 NE	8 NW	0.0 (90°Right)[2]

[5] Reseeded with 50 gallons after three hours.

Wind velocities, $\vec{W}$, were obtained from anemometers on the vessel or, in a few cases, on the northern end of Trestle A of the Chesapeake Bay Bridge and Tunnel. The anemometers were not intercalibrated, but were regularly serviced and similarly mounted from 15 to 20 meters above the water surface.

Slicks enlarged by spreading for a few hours after release and took various shapes, sometimes linear or pseudopodal, and often separated into sections. In white cap sea conditions, oil dissipation at slick edges was rapid, and slicks remained small. To track the slick and establish $\vec{S}$, the vessel was positioned at the downwind edge of the slick which was taken as the slick position. This procedure yielded a maximum slick motion.

The Coriolis deflection of $\vec{C}$ from $\vec{W}$ is approximately 20° in offshore areas at medium latitude, and decreases nearer shore. (Doebler, 1966; Hela, 1952; Mandlebaum, 1955). Since all water depths occurring in this study are less than 30 meters, deflections of $\vec{C}$ and $\vec{R}$ from $\vec{W}$ are assumed to be zero.

Wind generated surface currents require a few hours to reach maximum speed (James, 1968), but a direct coupling of $\vec{C}$ with $\vec{W}$ is assumed here. The study area is not suited to a check of the degree of coupling because there are frequent wind vector changes and rather large tidal current oscillations. Calculated wind factors are slightly overvalued, due to the wind-produced positive gradient of horizontal velocities near the water surface. The drogue did not measure current at the air-water boundary where the velocity is a maximum.

Figure 2 shows the relative wind factor plotted versus speed. There is apparently a functional dependence, with a wind speed intercept of approximately 7 knots. This wind speed must be exceeded to produce a significant difference between the surface current motion and the slick motion. For winds between 15 and 20 knots, the relative wind factor is about 1.3 percent, and may approach 2.0 percent at higher wind speeds.

Additional oil release studies would permit more precise establishment of the relative wind factor, but this precision will not be needed for oil cleanup purposes. Given that overall slick speed should be known to 0.25 knot, sufficient accuracy is realizable from a knowledge of surface currents, plus an approximate 1.3 percent of the wind speed additional for winds greater than 15 knots.

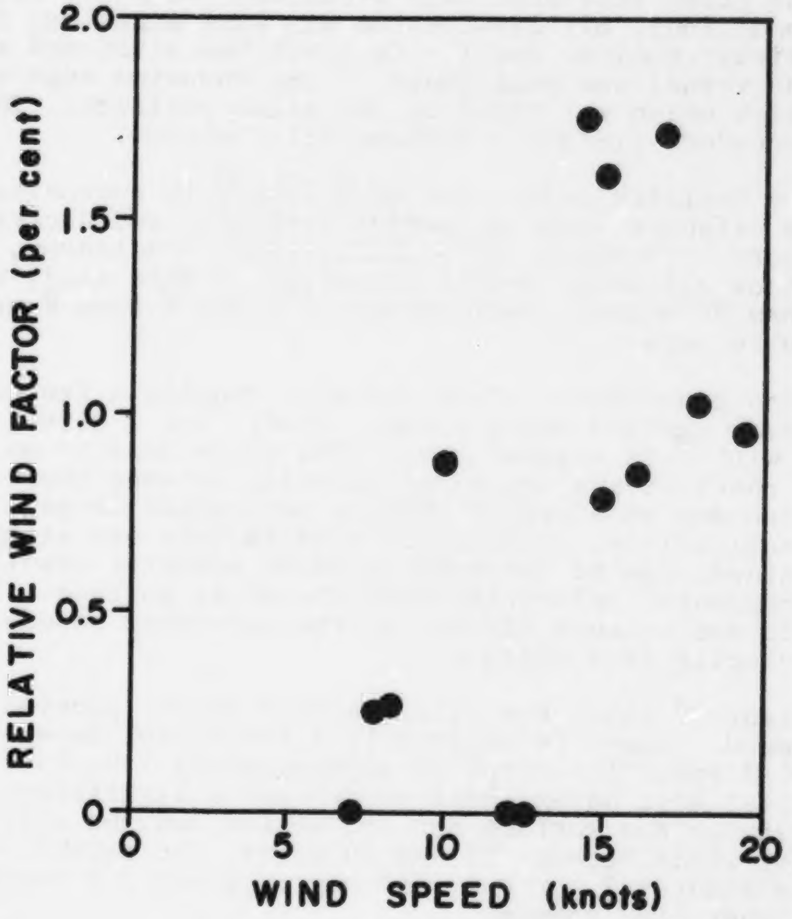

Fig. 2. **Relative wind factor versus wind speed from data in Table 2.**

Accurate predictions of oil slick motion require knowledge of local surface currents, tidal currents, oceanic circulatory currents and wind conditions. The error in prediction of oil slick motion is directly dependent on the quality of the available water current information and weather predictions. In areas of high potential oil spill threat, detailed long term surface current studies should be made. The current data would permit better protection of threatened coastlines.

Sufficiency of existing surface current information for prediction of oil slick motion near the Chesapeake Bay Bridge-Tunnel has been tested using the experimental releases in this region. Tidal currents were obtained from predictions of the U. S. Coast and Geodetic Survey (1969, 1970), which include the effect of average seasonal winds. Wind velocities were taken as measured, and several overall wind factor values were selected from the literature and experience obtained in this program.

These data were supplied to a computer program (Appendix 1) which predicted slick motion after a spill at a stated location and time. The current path is predicted under the assumption of uniaxial sine wave tidal oscillations and using inverse r^2 weight-averaging of tidal currents at U.S.C.&G.S. stations to estimate tidal currents at other positions in the region. Possible effects due to winds preceding the spill (James, 1968; Harrison and Pore, 1967; Johannessen, 1968; Jones and Bellaire, 1962; Bellaire, 1963) were not included in these predictions due to unavailability of information for lower Chesapeake Bay.

Figure 3 is a chart of the Chesapeake Bay entrance, showing observed slick motions and predicted current paths calculated with 0, 3, and 10 percent overall wind factors. In comparing predicted paths and actual slick motions, it should be realized that slicks follow the current path and are only slightly modified by the relative wind factor. The predicted paths do not match or bracket the observed motions. Discrepancies are not regular and amount to several miles in a single flood or ebb tide.

For Chesapeake Bay entrance, tidal currents permit predicting the general directions of slick travel but are inadequate for accurate prediction of oil slick trajectories. Better prediction will require analysis based on long time series observations of local currents and winds. It is doubtful that acquisition of these data could be financially justified for prediction of oil slick motion alone. If there are other environmental problems that also

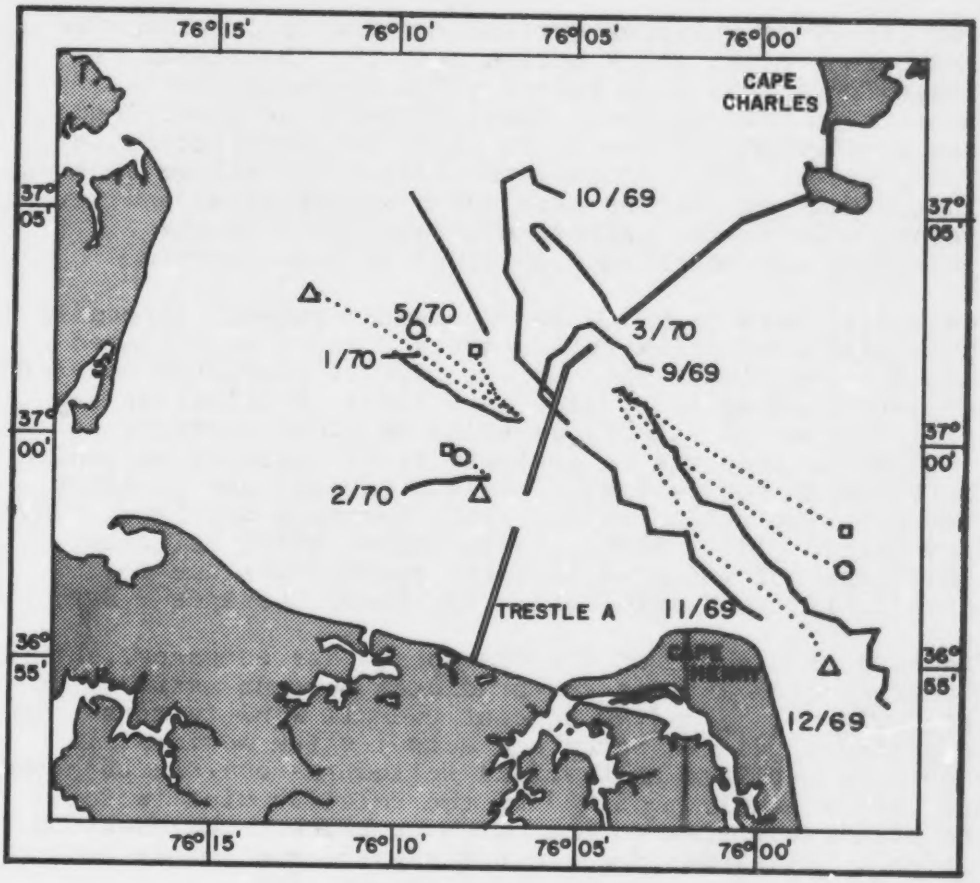
76° 15'
76° 10'
76° 05'
76° 00'
CAPE CHARLES
37° 05'
10/69
5/70
1/70
3/70
9/69
37° 00'
2/70
TRESTLE A
11/69
36° 55'
CAPE HENRY
12/69

Fig. 3. Oil slick trajectories at Chesapeake Bay entrance. Solid lines are observed trajectories, dotted lines are predicted paths with square, circle and triangle indicating zero, three and ten percent overall wind factor respectively.

require this series data, consideration should be given to installation of long term monitoring stations.

The oil slick motion prediction program was used to predict the path followed by oil on releases near Chesapeake Light Tower on August 12, 1970, December 3, 1970, April 26, 1971, August 3, 1971, and September 14, 1971.

Tidal current information for this area was obtained from Haight (1942) and U.S.C.G. tidal height tables for 1970 and 1971 by referring tidal currents at the light tower in hours after Greenwich transit of the moon to tidal heights and times at Hampton Roads on the spill dates. It is fortunate that tidal currents here are linear reversing and can be used directly in the program. The program is now being modified to accommodate radial tides which occur in other continental shelf areas. The tidal currents used here are based on more than a year of observations, so transient phenomena are quite well filtered.

The overall wind factor used in the program was 3.7 percent, a value suggested by our observations and the experiments of Schwartzberg (1971). The predicted and observed slick motion paths are given for each slick in Figures 4 through 8.

The predictions for the August 12, 1970, and December 3, 1970, releases are acceptably close to the observed motion. The predicted motion for April 26, 1971, is totally wrong, and on August 3, 1971, the direction but not the total displacement was correctly predicted. The observed path for September 14, 1971, made a sudden 90 degree course change that did not appear in the prediction.

Large deviations of predicted from observed slick motion were anticipated in the Chesapeake Light Tower vicinity, because tidal information was obtained 5 miles north of the present light tower, large scale current systems in the region are poorly known, spring and neap tide situations were not considered, the wind history prior to release was not available, and local surface currents were not obtained as current meters were not deployed. The predictions were surprisingly good in view of the above limitations. The simple program used here predicts motion fairly accurately in the absence of large scale current fields, excepting tides, generated outside the area of observation.

Research on oil slick motion is continuing, and releases in proximity to fixed current meters are being planned.

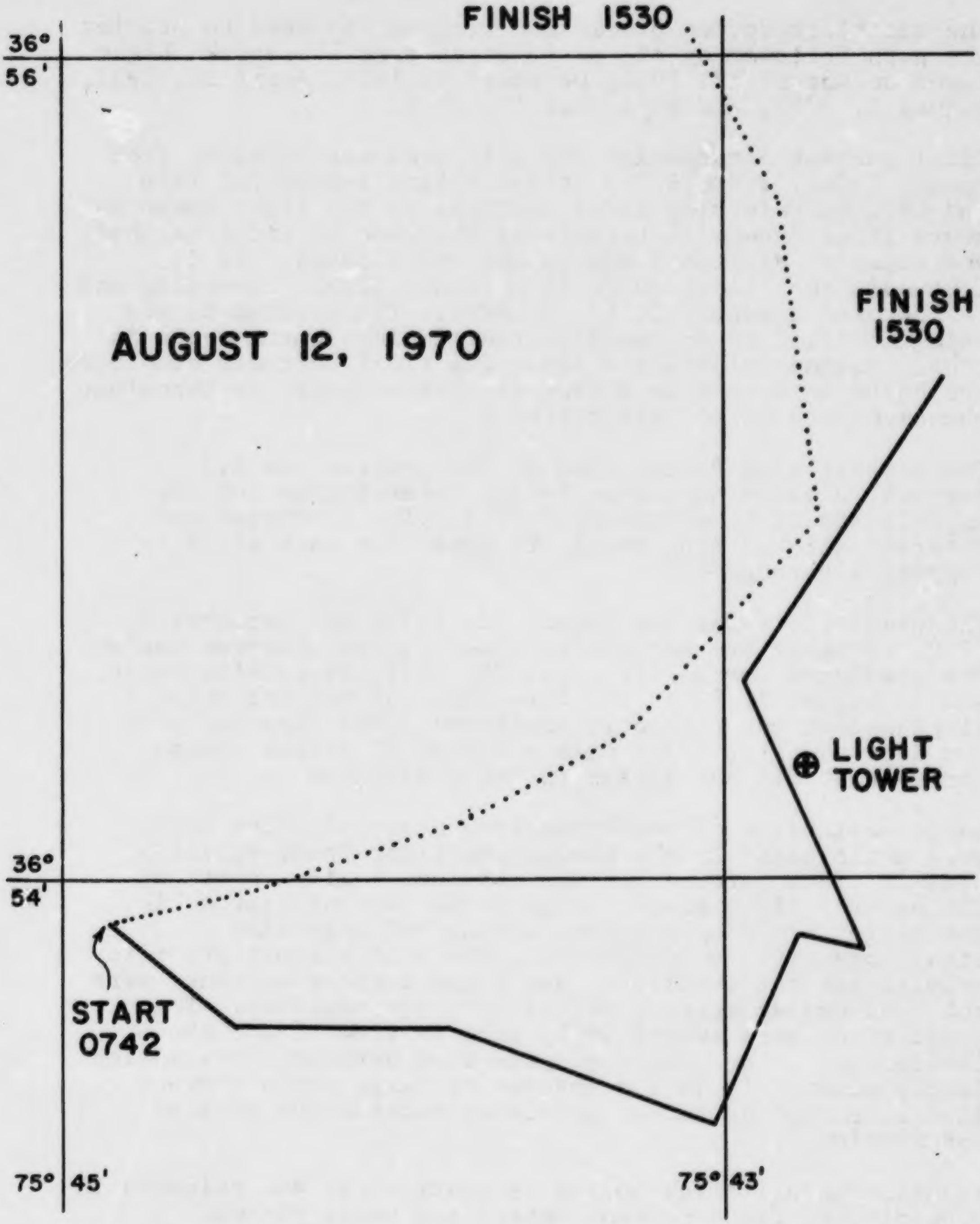

Fig. 4. Predicted (····) and observed (——) paths for Aug. 12, 1970, release.

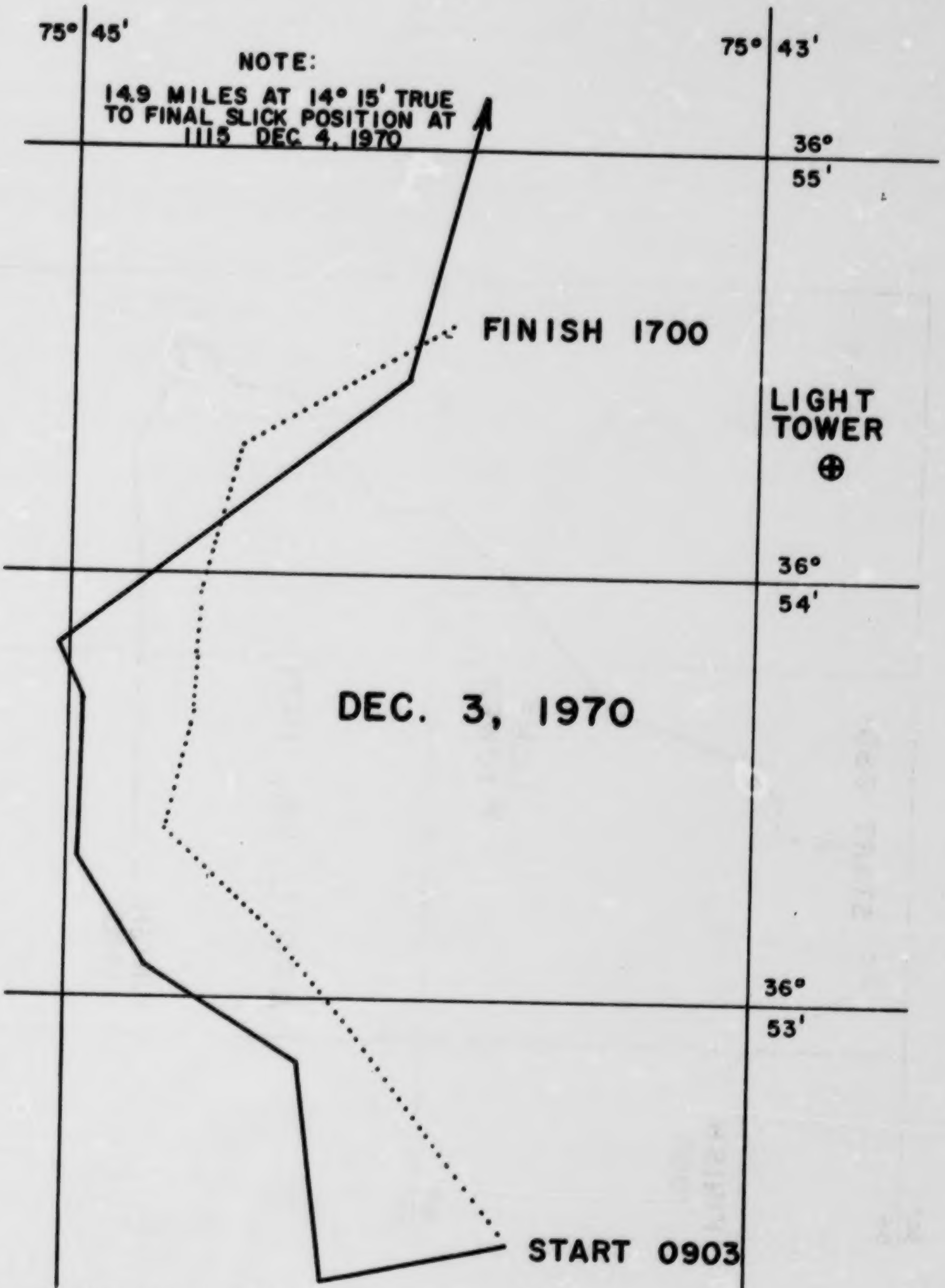

Fig. 5. Predicted (····) and observed (——) paths for Dec. 3, 1970, release.

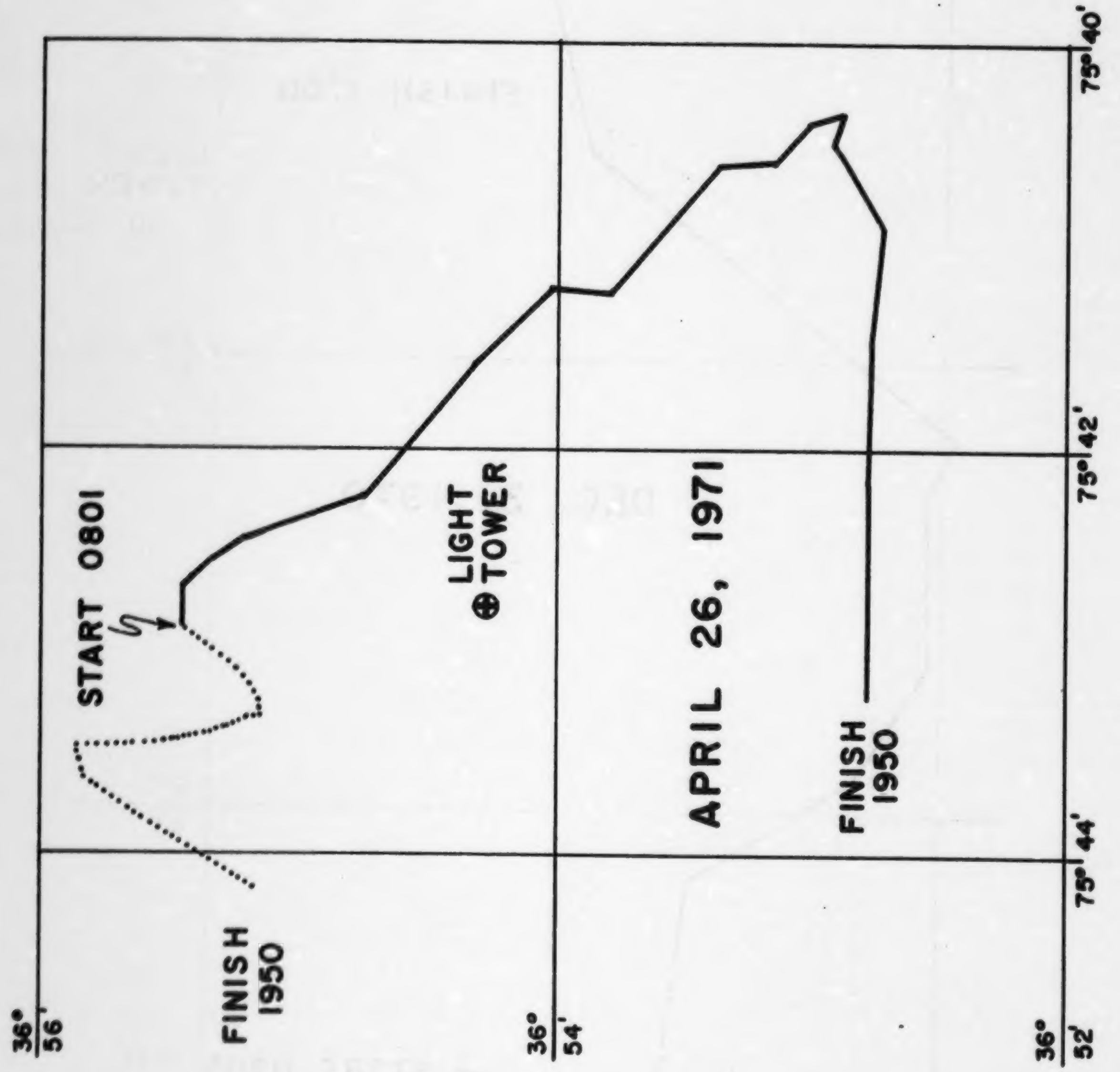
START 0801
LIGHT TOWER
APRIL 26, 1971
FINISH 1950
FINISH 1950
36° 56'
36° 54'
36° 52'
75° 40'
75° 42'
75° 44'

Fig. 6. Predicted (····) and observed (——) paths for April 26, 1971, release.

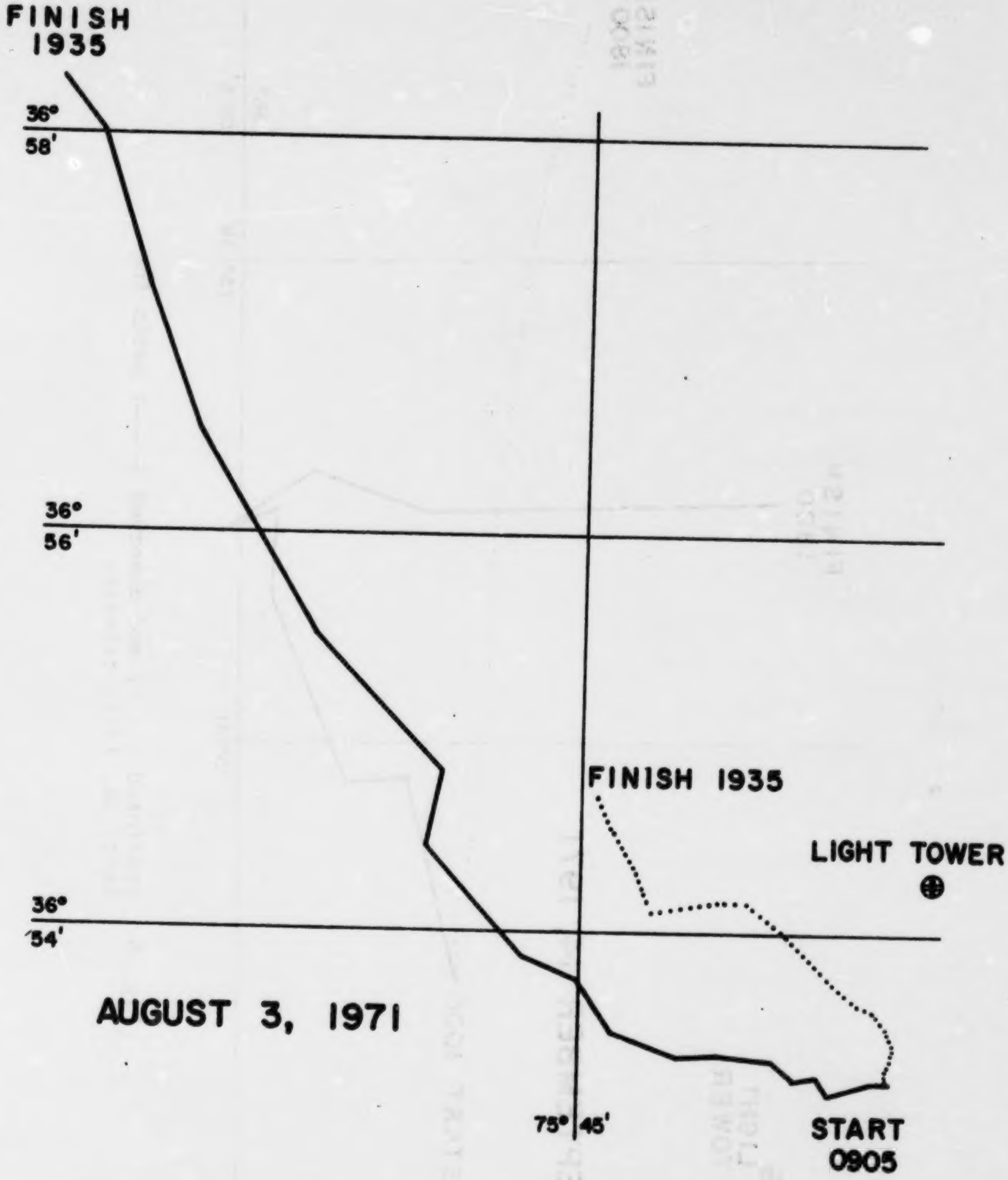
FINISH
1935
36°
58'
36°
56'
36°
54'
FINISH 1935
LIGHT TOWER
AUGUST 3, 1971
75° 45'
START
0905

Fig. 7. Predicted (....) and observed (——) paths for Aug. 3, 1971, release.

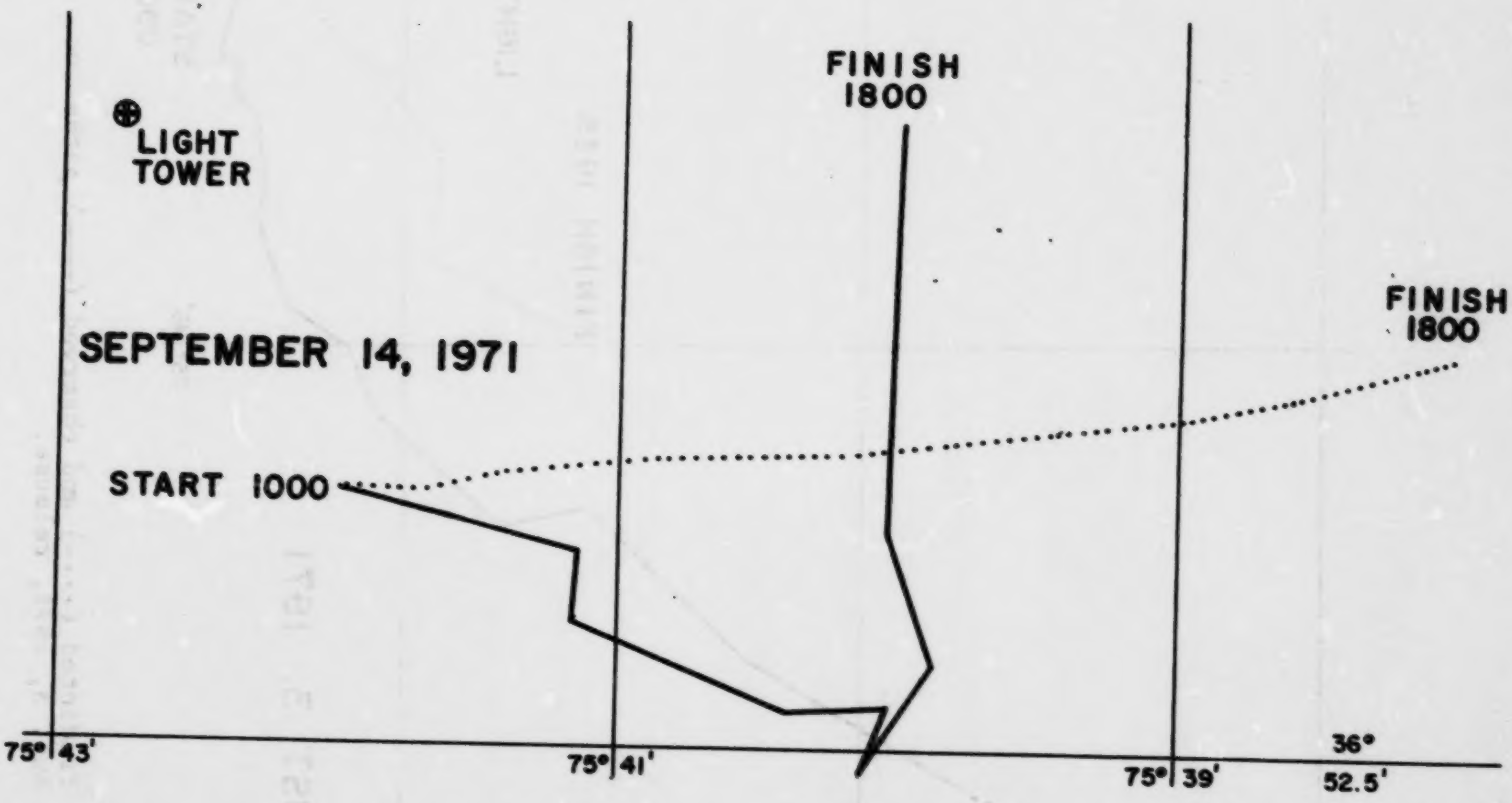

Fig. 8. Predicted (····) and observed (——) paths for Sept. 14, 1971, release.

Parachute drogues may be used to measure surface displacement of oil from the underlying water mass. The objective of this work is to develop a more complete system of equations for oil motion prediction. These equations will only be useful if concurrent wind and current data is available.

To implement a more accurate prediction than demonstrated above, an instant delivery current meter-anemometer system must be deployed at the spill site and data from the system telemetered to a computer which will use the data to make motion predictions. The spill must be at least 6 hours away from any beaching area in order for this type of prediction to be achieved.

If such a prediction system proves too costly, current surveys should be made to establish average large scale currents. Predictions based on these averages will be imperfect, but certainly better than what can now be achieved. Prediction of slick motion on the continental shelf is only possible where tidal currents are available, which limits any present predicting ability to a few selected regions.

SECTION V

INITIAL AGING OF FUEL OILS ON SEAWATER

INTRODUCTION

Fuel oils can be classified into two main types. The distillate fuels are the distilled fraction of a selected boiling range of crude petroleum. Representative distillate fuel oils are kerosene and diesel fuels, and No. 2 fuel oil. Residual fuel oils, on the other hand, are generally mixtures of the asphaltic residue from the distillation of crude petroleum with selected distillate fractions of the crude petroleum. The exact formula varies from one producer to another and often varies between batches from the same producer. ASTM specifications for these residual fuels, such as No. 4, 5, and 6 (Bunker C) fuel oils are concerned primarily with the viscosity range, and permit large variations in composition.

Oil spilled on the water undergoes a process called "aging" or "weathering," which has the effects of reducing the total volume of oil, and of changing its physical characteristics. This aging is the result of at least four distinct processes:

1.) Evaporation of volatile constituents.

2.) Dissolution of oil constituents into the water column.

3.) Microbial degradation or modification.

4.) Photochemical oxidation.

Little is known about the effect of light on oils, but photochemical oxidation of individual hydrocarbons usually requires considerable amounts of ultraviolet irradiation in the vapor phase. The effect of photochemical oxidation is expected to be minimal for oils in relatively thick films or clumps. Microbial degradation (Kator, 1971), though an important process in the ultimate fate of oil spilled on the sea, requires seeding and addition of nutrients for rapid effect. This mechanism should not be an important factor in the initial aging of oil spilled on the sea for at least the first 48 hours. Thus, evaporation and dissolution will be major mechanism of initial aging of fuel oil on seawater.

Information on the initial aging of fuel oils can be valuable for the estimation of the remaining volume of an oil slick by the time men and equipment can be assembled to deal with it. Additionally, one can predict the change of character of the spilled oil from its residence time at sea, and estimate the amount of oil components which have been released to the atmosphere by evaporation, and to the water column by dissolution.

Two different approaches have been utilized in this study of initial oil aging. The primary line of study was the observation and analytical sampling of small volume spills of No. 2, 4, and 6 fuel oils at sea. Twelve releases, ranging from 60-200 gal. of oil, four for each oil type, were conducted under a variety of climatic conditions. Nine releases were made in the Atlantic Ocean in the vicinity of the Chesapeake Light Tower, and three releases, one of each oil type, were made in the more sheltered waters of the Chesapeake Bay, near the York River entrance. Samples of oil were taken from the slicks at regular intervals and preserved for later analysis.

A laboratory aging experiment for each oil type was carried out as an adjunct to the field studies. The experiment consisted of periodic sampling of the effluent air stream and aqueous phase of a carboy bubbler apparatus in which air was bubbled through an oil film floating on artificial seawater.

METHODS AND MATERIALS

Fuel oils used in this study were procured locally. No. 2 fuel oil was a straight run distillate derived, as far as can be determined, from various Texas crudes. It had a boiling range of 170-370°C/760 torr, determined by actual distillation under reduced pressure in a distillation unit with a 24" Widmer column constructed according to specifications from the ESSO Baytown Refinery. Head temperatures at reduced pressure were converted to atmospheric, using tables from the ASTM Method for Distillation of Crude Petroleum (D2892-70T). Boiling range was confirmed by the ASTM Test for Boiling Range by Gas Chromatography (D-2887-70T). A boiling range composition is included in Figure 9. The aromatic character of this fuel was determined by the ASTM Fluorescent Indicator Adsorption Test (D-1319-70).

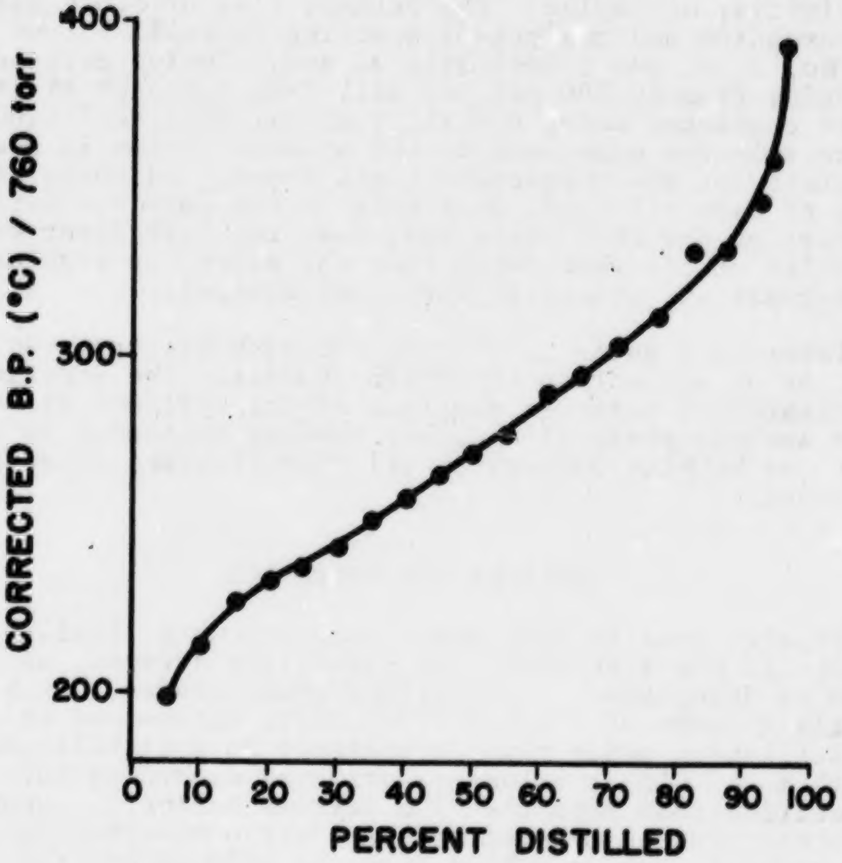

Fig. 9. Boiling range composition of No. 2 fuel oil.

No. 4 and 6 fuel oils, purchased from the Humble Norfolk Terminal, were formulated by the Lago Oil and Transport Co., Aruba, Netherlands Antilles, as C401 and C552, respectively. Both were derived from tar produced from mixtures of Venezuelan crudes by thermal cracking and blended with diluents composed of a number of refinery streams to achieve an appropriate viscosity. Both fuel oils had initial boiling points near 170°C/760 torr, and actual reduced pressure distillation showed no major discontinuities in the boiling range composition for either fuel. Boiling range compositions are shown in Figures 10 and 11. The aromatic character of each was determined by the Fluorescent Indicator Adsorption Test (ASTM D-1319-70) on the distillate fraction, b.p. 170-270°C/760 torr. This test is not possible for the whole fuel oils, which contain considerable proportions of high molecular weight components. The aliphatic and aromatic portions of some fractions of the oil distillate were separated on a silica gel column, eluted with pentane to remove the aliphatics, then with benzene to remove the aromatics from the column. Progress of the separation was monitored with gas chromatography.

In the field studies, oil samples were collected in a separator scoop which allowed the partial separation of water from the oil. Sample collection was biased toward the thicker oil layers in the slick. Oil samples, together with small volumes of unseparated water were stored in quart Mason jars with aluminum foil lid liners. Samples in the jars were then frozen and temporarily stored in portable ice chests packed with dry ice. The samples were later stored in a commercial freezer chest until analyses could be made.

Analyses were carried out by gas chromatography. Oil samples were treated in the following manner. No. 2 fuel oil samples were chromatographed directly. No. 4 and 6 fuel oil samples, which were too viscous to permit direct syringe injection, were injected in pentane solution. To aliquots of frozen samples weighing approximately 5 g each, 30 ml of Baker "Baker Grade" pentane was added, and the mixture was stirred and triturated until a homogeneous solution or suspension was achieved. The solutions or suspensions were each gravity filtered through Whatman #42 filter paper to remove precipitated asphaltenes and other pentane insoluble matter. The filtrates were then stored in glass-stoppered flasks and portions of these filtrates were then chromatographed.

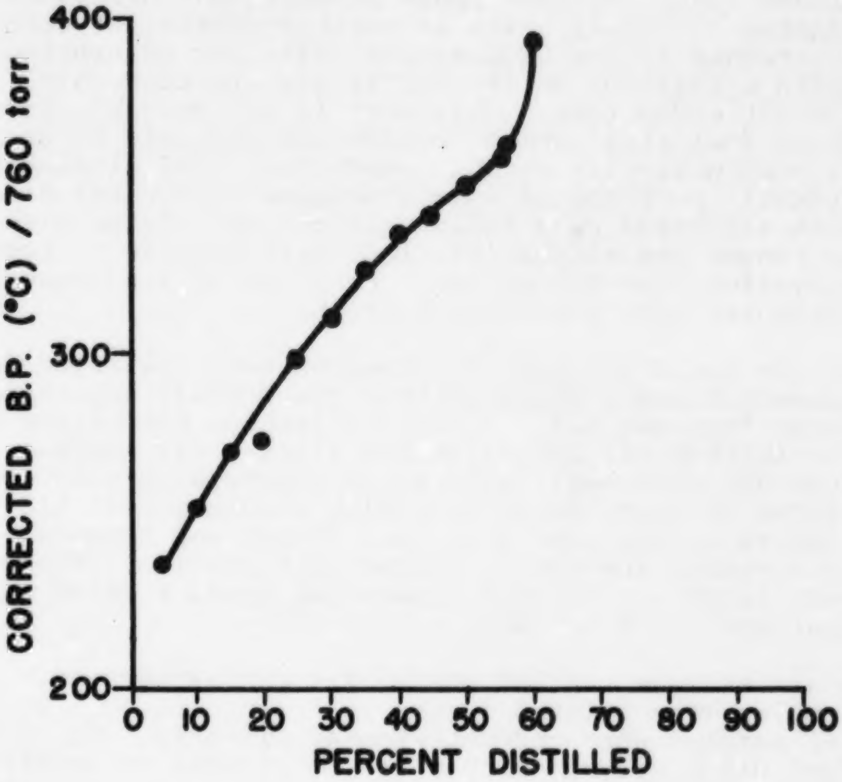

Fig. 10. Boiling range composition of No. 4 fuel oil.

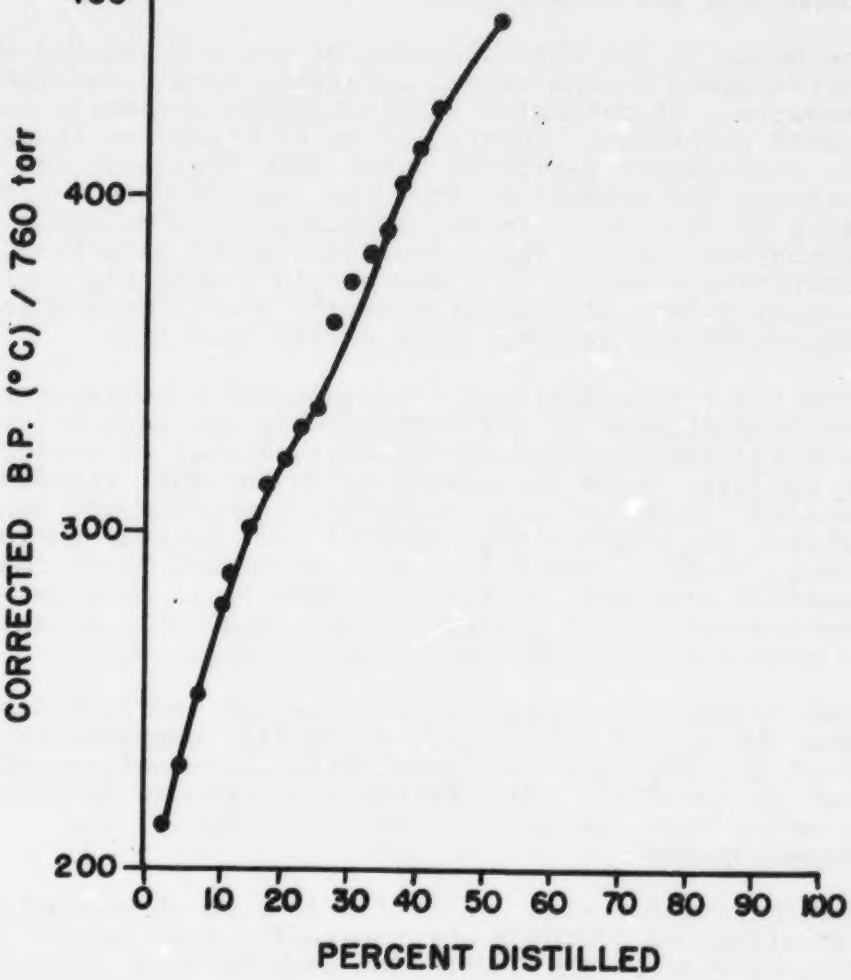

Fig. 11. Boiling range composition of No. 6 fuel oil.

Gas chromatography was done using a Perkin-Elmer Model 900 Gas Chromatograph fitted with dual 1/8" x 6' copper columns packed with 5% SE 30 or 60/80 mesh Chromosorb P-NAW, and with flame ionization detectors. The carrier gas was helium, at a nominal flow rate of 20 ml/min, and the temperature was programmed from 100-280°C at a rate of 4°C/min, and permitted to hold at 280°C until all volatile components had been eluted.

The peaks in the chromatograms of the oil samples which corresponded to the normal paraffins were determined by comparison of retention times with the authentic samples of normal paraffins. Interpolation of retention times between the even-carbon paraffins which were available was used to estimate the retention times for the odd carbon paraffins. Aging of the fuel oils was followed by calculating this percentage loss of the individual normal paraffins, which constitute a series of compounds in rather high initial concentrations with boiling points evenly distributed throughout the boiling range of the fuel oils.

Quantitative analysis of normal paraffin concentration was accomplished by determination of the peak height for each individual compound relative to that of n-eicosane ($\underline{n}$-$C_{20}H_{42}$), which was chosen as an internal standard because: 1) it has a sufficiently low vapor pressure at ambient temperature that minimal loss by evaporation will occur; 2) it is quite insoluble in water; 3) of the possible compounds in the oil which could meet the first requirement, it is present in all three oils in sufficient concentration for the peak height comparison.

Peak heights were considered to be the vertical distance from the top of the peak to a baseline constructed by drawing a straight line connecting the shoulders of the peak in question. This baseline was generally, but not in every case, tangent to the background of the chromatograms.

Peak height for each n-paraffin in each chromatogram were normalized by dividing the n-paraffin peak height by that of n-eicosane. The normalized peak heights of each n-paraffin were then divided by the normalized peak height of the corresponding n-paraffin in the chromatogram of the unaged oil to give $(\%C_i)_t$, the percentage of n-paraffin remaining in the oil sample taken at time t. The following equation expresses this procedure:

$$(\%C_i)_t = 100 \times \frac{[C_i]_t}{[C_{20}]_t} \times \frac{[C_{20}]_{t=o}}{[C_i]_{t=o}}$$

where $[C_i]_t$ represents the peak height of the normal paraffin C_iH_{2i+2} at time t.

The reproducibility of this procedure was tested by calculating $(\%C_i)_t$ using chromatograms from repetitive injections of the same sample of No. 2 fuel oil. Successive determinations showed that $(\%C_i)$ varied ±3% of the value determined from the initial sample.

The bubbler experiments were carried out using a specially constructed apparatus (Figure 12). Air from an aquarium pump at the rate of 2 l/min was passed through a tubular filter containing equal volumes of 16 mesh indicating silica gel and activated carbon granules to remove contaminating substances from the sweep gas. The filtered air was then bubbled up through a glass tube at the bottom of a carboy containing 30 ml of oil on 10 l of artificial seawater (33‰ NaCl). An opening at the bottom of the carboy permitted removal of the seawater for analysis without danger of contamination from the surface film. The effluent air stream from the bubbler was then passed through a plug of extra fine glass wool to remove small droplets of water and oil, and then into a concentric-type vapor trap, which was chilled in a dry ice/acetone cooling bath.

In operation, the bubbler was permitted to run until the ice crystals in the vapor trap began to reduce the sweep gas flow rate. The trap was then removed from the cooling bath and warmed to room temperature, causing the obstruction to melt and collect at the bottom of the trap. This procedure of trapping and warming was repeated as necessary. At selected intervals the trap contents were removed, and extracted 5 times with 1 ml of pentane. The combined extracts were allowed to evaporate to a volume of 4 ml and transferred to a 5 ml and the sample used for gas chromatographic analysis. Samples of the seawater layer were removed at the termination of the bubbler aging, filtered through a plug of extra fine glass wool to remove suspended oil droplets, and extracts were allowed to evaporate at room temperature to a volume of less than 1 ml, then transferred to a 3 ml volumetric flask and adjusted to exactly 3 ml. This sample was used for gas chromatographic analysis.

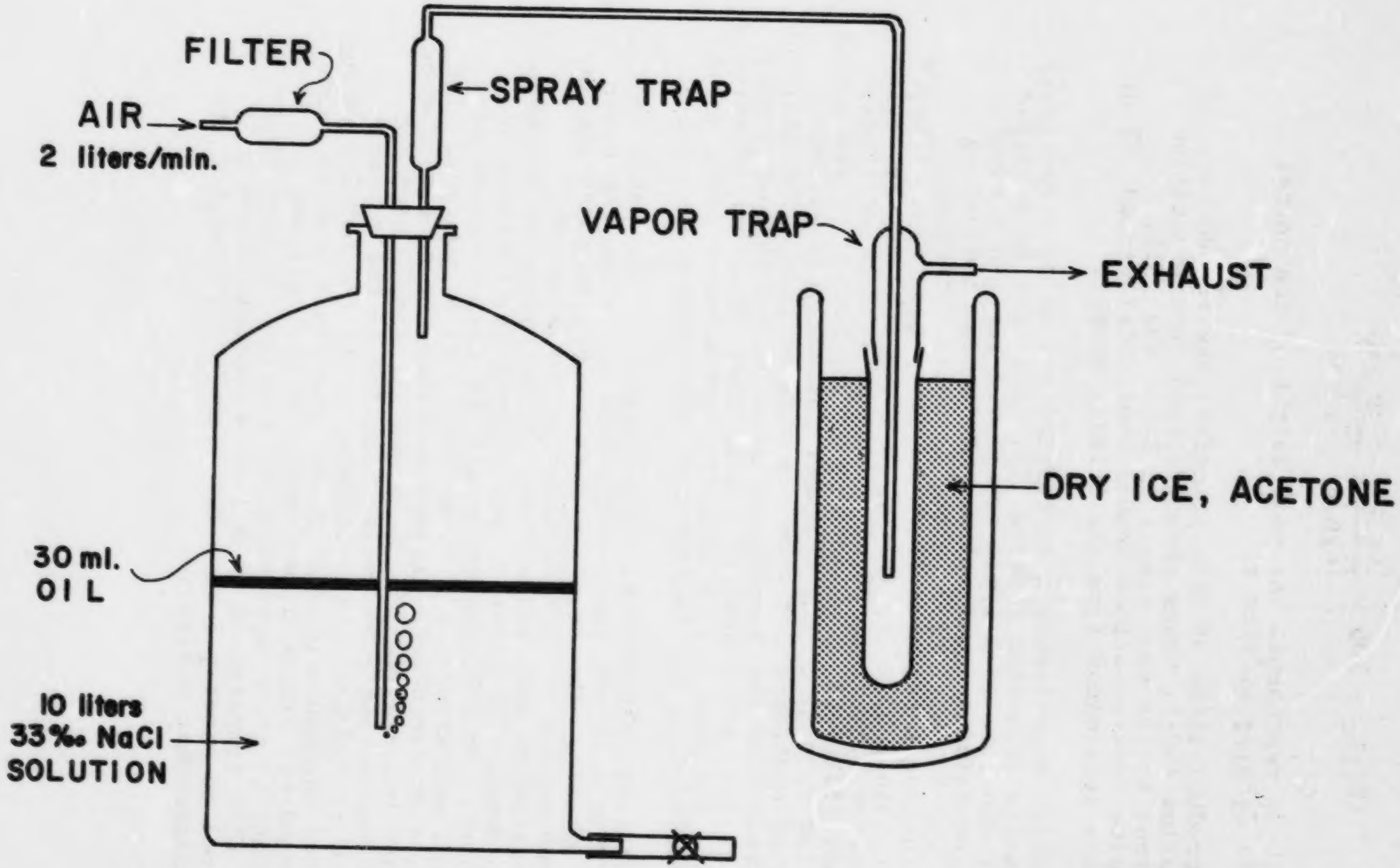
FILTER
AIR
2 liters/min.
SPRAY TRAP
VAPOR TRAP
EXHAUST
DRY ICE, ACETONE
30 ml.
OIL
10 liters
33‰ NaCl
SOLUTION

Fig. 12. Bubbler assembly for oil film aging.

Samples from both the vapor trap and the seawater layer, prepared as above, were chromatographed on a Perkin-Elmer Model 900 Gas Chromatograph fitted with dual 1/4" x 3' copper column packed with 5% SE 30 on Chromosorb W-HMDS treated support. The temperature was programmed from 50-300°C at 8°/min, which produced the required resolution for the ASTM Boiling Range Distribution of Petroleum Fraction by Gas Chromatography (D-2887-70T). Samples of the vapor trap were analyzed in the following manner. A plot of boiling point (atmospheric) versus retention time was constructed from the chromatogram of a mixture of authentic n-paraffins (Figure 13). Then, initial and final boiling points were calculated according to the ASTM D-2887-70T test, by planimetry of chromatograms of vapor trap samples. By comparison of the total area under the sample chromatograms with the area under the peak of the n-octadecane concentration standard chromatogram, the total weight of the oil-derived hydrocarbons in the pentane solution was calculated. The following formula illustrates the calculation:

$$\text{oil weight} = \frac{\text{Peak area oil}}{3.69\ \text{Peak area}/\mu\text{g}\ \underline{n}\text{-}C_{18}} \times \frac{\text{Volume Pentane extract}}{\text{Volume injected}}$$

The factor 3.69 in the equation derives from a calibration run, in which a standard solution of 9.704 g/1 of n-octadecane in pentane produced a ratio of 3.69 peak area units per µg n-octadecane.

Samples produced by extraction of the seawater layer were chromatographed under similar conditions to those of the vapor trap, and the area under the chromatogram was integrated by planimetry. The weight of oil hydrocarbons in the pentane extract was determined by a formula analogous to that above:

$$\text{oil weight} = \frac{\text{Peak area oil x Volume Pentane extract}}{2.75\ \text{Peak area}/\mu\text{g naphthalene x Volume injected}}$$

The factor 2.75 is derived from the calibration chromatogram, in which a standard solution of 1.354g/1 of naphthalene in pentane produced an integrated peak area of 2.75 area units per µg of naphthalene. Naphthalene was chosen for this standard because the oil components extracted from the seawater appeared to consist of naphthalene and its derivatives.

In certain instances, large volumes of 10 µl or more of the pentane extracts of the seawater layer were injected into the gas chromatograph fitted with a fraction splitting accessory. Samples corresponding to major component peaks

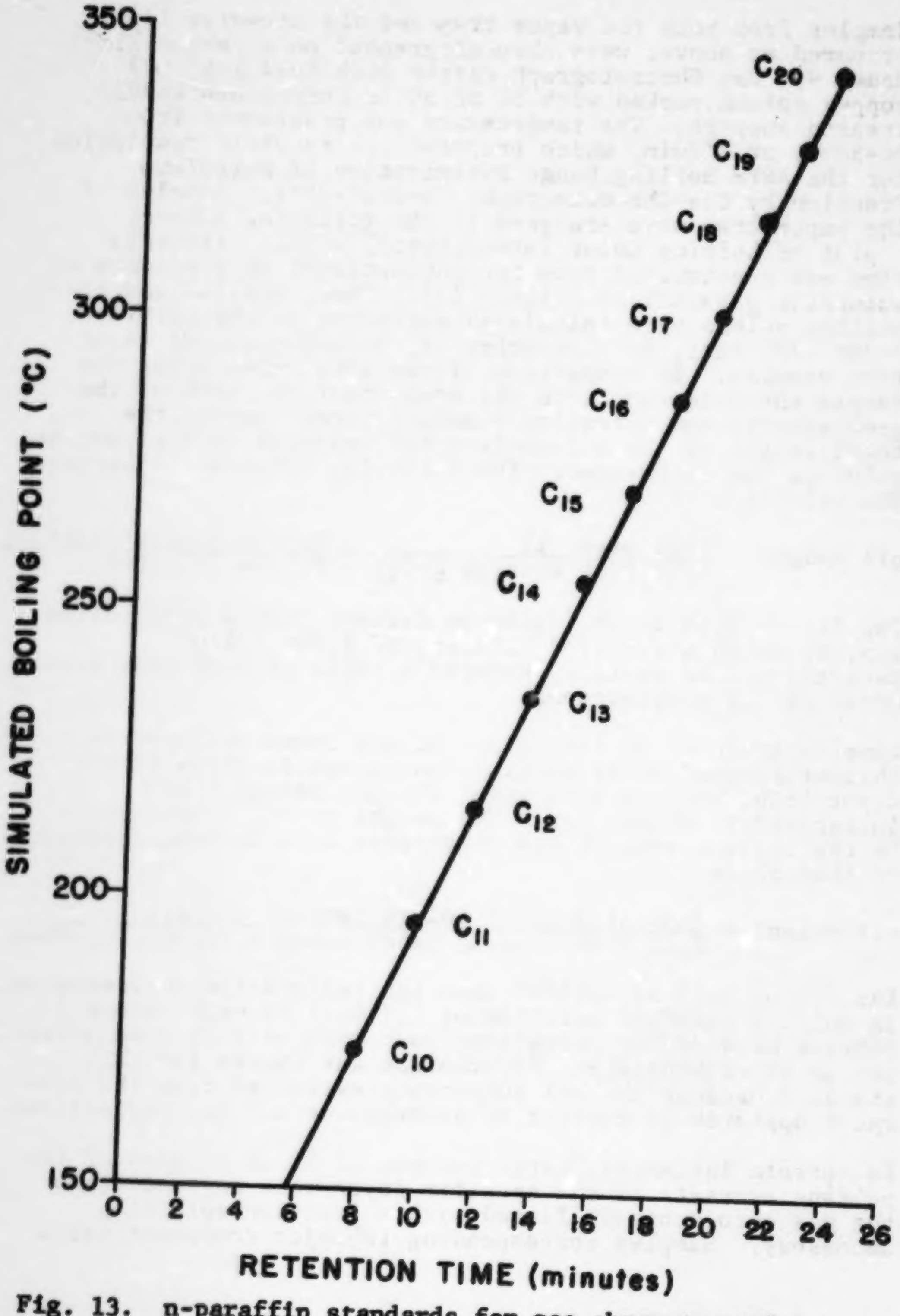

Fig. 13. n-paraffin standards for gas chromatography.

were condensed in 2-3 mm diameter glass capillary tubing. These sample tubes were sealed off, and used for mass spectrometric analysis. The tubes were broken open, and fitted into the solid sample introduction device of a CEC 21-104 Mass Spectrometer, and the 70eV mass spectrum recorded. Although the mass spectroscopic study of the chromatographically separated components was incomplete, due to poor separations, basic structural units were identified. Further investigation of these dissolved components should be carried out when suitable instrumentation becomes available.

An additional experiment was designed to determine the rates of which certain representative aromatic compounds are scrubbed out of aqueous solution in the bubbler apparatus. Ten liters of 33‰ aqueous NaCl solution was stirred for 24 hrs with a mixture of 5 g each of cumene (i-propylbenzene), naphthalene, and 1-methyl naphthalene. The excess organics were then removed, and the aqueous solution filtered through a plug of extra-fine glass wool to remove suspended droplets of organic compounds. The seawater was then returned to the bubbler apparatus. After removing a time-zero sample, the air sweep, at a rate of 2 l/min was initiated. Samples were removed at periodic intervals. The samples, 1 l each, were extracted four times with 10 ml of pentane, and the combined extract reduced in volume by evaporation at room temperature to less than 3 l. The extracts were then transferred to 3 ml volumetric flasks and adjusted to exactly 3 ml. The concentrations of the three organic components in the extracts were determined by gas chromatography, comparing the peak areas to those of known concentrations of naphthalene.

RESULTS AND DISCUSSION

Twelve experimental releases were conducted, employing the three fuel oil types, No. 2, 4, and 6 (Bunker C) fiel oils. Samples of oil from the slicks were collected at regular intervals as long as possible. Because of the low solubilities of the oil components and the enormous dilution factor involved, sampling of the water column beneath the slick was not attempted. The samples obtained were analyzed by gas chromatography for the relative amounts of the normal paraffin hydrocarbons, which were selected to be model oil components. The n-paraffins consist of a homologous series of compounds in these fuel oils, whose members produce distinctive, sharp peaks at regular intervals throughout the boiling range in the gas chromatograms of oil samples.

Results of the n-paraffin analyses for the twelve field releases are given in Tables 3(a) through 3(l). The entries in the tables are the percentage of the given n-paraffin remaining in the oil at time t: $(\%C_i)_t$. The average local conditions during the sampling period are also recorded.

The $(\%C_i)_t$ for a given n-paraffin in an oil slick would be expected to decrease in some sort of monotonic fashion with time. Inspection of the tables show, however, that fluctuations occur, and in some instances, the $(\%C_i)_t$ is greater than 100%. No reasonable mechanism can account for a net increase of the n-paraffin content of an oil slick, so such anomalously high values must not reflect the true concentrations. Several factors inherent in the method of analysis seem likely to contribute to such errors. One problem is the necessity to use four separate peak height measurements in the calculation of $(\%C_i)_t$. A test of reproducibility using a single oil sample showed that $(\%C_i)_t$ could be determined to ±3%; however, since the estimation of peak heights is not better than ±5% for most peaks, the maximum uncertainty in the $(\%C_i)_t$ would be propagated to ±20% by the mathematical treatment. Another problem associated with the quantitative gas chromatography of fuel oils is the fact that the n-paraffin peaks are not completely separated from the background of aromatic, isoprenoid, isoparaffin and naphthene hydrocarbons. Peak heights are measured from the peak maximum to an estimated baseline, which depends upon the detailed nature of the background. Although a highly reproducible baseline estimate can be made for unaged samples, problems arise when the concentrations of the various petroleum compounds change by aging. Then, changes in overlapping and underlying peaks greatly affect the estimation of the n-paraffin baseline, and hence the determination of peak height.

A final possible source of error comes from the variation of sampling location in the slick itself. Since a thin oil film will age more rapidly than a thicker one, the thickness of the oil being sampled has considerable import. In actual practice, the samples were collected from the thickest layers of the slick that could be found. It was not possible to tell whether a particular layer had been thick since the spill, or was the result of coalescence of thinner films.

Table 3(a). **Fuel Oil Aging - Loss of Normal Paraffin**
Location: Chesapeake Light Tower
Oil: 200 gallons, No. 6 Fuel Oil
Release: 0900 hrs, EST, 12/3/70
Water Temp: 13°C. Air Temp: 60°F.

% Paraffin	Time After Release (hrs) 1:00	2:00	3:00	4:00	5:45	24:15	26:30
C9	156.5	70.7	119.6	70.7	32.1	n.d.	n.d.
C10	158.0	65.3	173.2	94.2	91.0	n.d.	n.d.
C11	101.8	69.9	102.6	86.1	61.2	n.d.	n.d.
C12	118.9	97.8	140.5	106.4	105.5	n.d.	n.d.
C13	109.0	106.0	142.4	103.8	122.5	16.0	25.0
C14	105.0	102.4	116.4	104.8	113.0	31.4	43.5
C15	118.2	109.8	132.7	128.6	123.5	56.3	74.1
C16	100.4	101.2	116.1	109.8	108.0	70.3	85.6
C17	101.4	105.5	115.0	106.2	107.2	91.2	103.8
C18	98.2	102.2	100.2	95.7	95.7	95.7	98.1
C19	99.5	102.9	106.7	103.4	101.1	92.8	101.5
C21	101.2	102.4	98.6	111.3	110.4	104.3	107.8
C22	102.6	103.8	101.7	103.7	106.7	102.6	103.1
C23	99.4	129.0	96.6	98.0	95.2	110.1	103.8
C24	102.5	n.a.	113.0	119.4	107.2	106.3	110.7

n.a. = not available

n.d. = not detected

Table 3(b). Fuel Oil Aging - Loss of Normal Paraffin
Location: Mid-Chesapeake Bay/New Point Comfort
Oil: 66 gallons No. 6 Fuel Oil
Release: 0830 hrs, DST, 6/23/71
Water Temp: 76°F. Air Temp:

% Normal Paraffin	Time From Release (hrs) 2:10	4:10	6:10	8:10	10:10	12:10	26:00	28:00	30:00
C9	63.6	4.2	9.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
C10	71.4	10.1	26.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
C11	88.1	19.2	48.0	n.d.	5.4	n.d.	n.d.	n.d.	n.d.
C12	102.4	41.1	78.6	11.1	32.7	12.8	n.d.	n.d.	n.d.
C13	107.5	51.3	86.3	30.7	52.1	35.1	2.6	n.d.	n.d.
C14	61.6	145.9	114.0	118.3	167.2	137.4	23.3	7.7	8.8
C15	104.2	94.1	102.3	87.6	99.4	89.8	26.8	26.1	13.6
C16	105.9	96.8	99.8	97.0	98.3	94.7	31.3	39.5	27.6
C17	103.5	101.7	105.4	106.6	100.9	99.5	76.4	71.5	70.7
C18	100.8	93.1	89.3	94.4	79.6	83.9	75.7	72.9	72.0
C19	103.2	97.0	99.1	100.6	88.7	91.9	94.9	87.1	85.1
C21	96.7	95.5	97.1	101.7	90.5	89.5	90.7	92.3	93.6
C22	99.5	100.4	98.3	105.3	95.2	92.9	99.3	99.4	100.5
C23	113.2	111.0	110.8	121.9	105.4	102.4	110.6	112.4	111.8
C24	102.3	98.7	99.7	105.1	90.9	88.6	93.1	96.2	94.0
C25	104.2	94.1	97.4	105.1	86.6	89.8	96.7	95.1	95.2

Table 3(c). **Fuel Oil Aging - Loss of Normal Paraffin**
Location: Chesapeake Light Tower
Oil: 200 gallons No. 6 Fuel Oil
Release: 1000 hrs, DST, 9/14/71
Water Temp: 23.8°C. Air Temp: 74°F.

% Normal Paraffin	Time After Release (hrs) 2:15	4:15	6:00	9:00	23:00	25:00
C10	24.5	n.d.	n.d.	n.d.	n.d.	n.d.
C11	14.1	6.2	n.d.	n.d.	n.d.	n.d.
C12	37.6	22.9	9.1	9.7	n.d.	n.d.
C13	60.0	43.3	25.0	32.4	n.d.	n.d.
C14	85.2	72.2	56.1	60.9	n.d.	n.d.
C15	88.0	82.8	69.5	81.2	11.3	5.2
C16	98.0	94.7	85.6	90.4	18.2	18.1
C17	94.9	91.1	86.7	94.0	36.8	27.8
C18	95.6	106.0	98.1	100.6	70.7	61.4
C19	100.6	97.5	95.9	97.9	85.9	81.7
C21	101.5	100.5	100.5	102.7	104.4	108.3
C22	99.1	98.3	98.2	97.1	101.7	105.7
C23	101.4	98.8	98.8	102.7	107.4	108.3
C24	n.a.	103.1	101.3	103.1	110.6	110.3
C25	n.a.	104.8	103.8	104.2	112.5	109.8

Table 3(d). **Fuel Oil Aging - Loss of Normal Paraffin**
Location: Chesapeake Light Tower
Oil: 200 gallons No. 6 Fuel Oil
Release: 1015 hrs, DST, 10/13/71
Water Temp: 71°F. Air Temp: 75°F.

% Normal Paraffin	Time After Release (hrs)				
	2:15	4:30	6:15	22:15	24:15
C10	n.d.	n.d.	n.d.	n.d.	n.d.
C11	69.9	n.d.	n.d.	n.d.	n.d.
C12	20.1	11.2	9.7	n.d.	n.d.
C13	37.2	27.2	35.6	n.d.	n.d.
C14	61.8	56.3	63.4	9.2	14.5
C15	73.3	74.7	81.5	36.8	40.8
C16	85.1	86.2	82.3	61.9	66.9
C17	91.5	95.4	94.5	76.7	79.4
C18	102.4	96.4	93.6	91.9	89.7
C19	98.7	96.5	96.0	92.8	93.1
C21	102.2	101.2	102.1	97.2	97.3
C22	99.2	97.0	100.3	101.6	102.1
C23	106.0	100.2	100.0	99.8	98.2
C24	117.7	107.7	107.5	110.6	101.2
C25	117.7	111.0	104.5	118.8	102.9
				110.9	104.8

Table 3(e). Fuel Oil Aging - Loss of Normal Paraffin
Location: York River Mouth
Oil: 200 gallons No. 4 Fuel Oil
Release: 0900 hrs, EST, 11/6/70
Water Temp: 15.4°C. Air Temp: 60°F.

% Normal Paraffin	Time After Release (hrs) 1:00	1:50	3:00	4:00	5:00	6:00	7:00	8:00
C10	117.8	73.7	71.8	55.9	59.5	9.8	n.d.	n.d.
C11	93.0	87.8	93.9	84.7	100.9	45.1	31.6	26.3
C12	98.9	103.5	106.4	91.4	147.7	94.3	50.0	34.5
C13	99.9	100.6	100.9	100.8	107.3	95.7	74.2	63.3
C14	126.0	115.3	118.2	116.9	124.1	103.8	113.0	125.7
C15	105.6	105.7	103.8	103.0	114.9	106.4	95.2	78.9
C16	106.7	104.2	107.3	104.6	109.6	103.6	104.8	117.3
C17	108.5	103.5	95.9	104.6	100.2	97.5	109.7	125.9
C18	107.5	117.2	105.6	105.8	99.4	99.9	103.8	107.1
C19	106.4	104.3	105.3	106.9	97.7	97.8	109.5	111.4
C21	102.8	101.7	106.0	105.8	98.7	101.5	106.5	109.8
C22	99.2	99.3	102.3	101.8	93.2	98.3	103.5	104.8
C23	101.1	101.6	101.8	102.6	92.9	97.5	100.5	91.5
C24	105.0	109.7	112.2	109.0	98.9	116.5	102.2	99.5
C25	95.4	104.3	96.9	99.1	92.3	98.2	101.8	112.2

Table 3(f). Fuel Oil Aging - Loss of Normal Paraffin
Location: Chesapeake Light Tower
Oil: 200 gallons No. 4 Fuel Oil
Release: 0730 hrs, EST, 1/22/71
Water Temp: 3.85°C. Air Temp: 47°F.

% Normal Paraffin	Time After Release (hrs)								
	1:00	2:00	3:00	4:00	5:00	6:00	7:00	8:00	9:00
C11	20.0	155.8	20.0	n.d.	75.1	144.8	79.3	5.0	5.2
C12	54.3	102.0	50.0	2.4	80.5	130.5	91.4	74.3	81.0
C13	49.4	97.8	76.8	45.5	87.9	84.4	93.5	91.1	85.3
C14	94.9	96.3	91.2	75.8	93.9	97.2	83.3	87.3	89.0
C15	96.7	88.7	95.1	88.9	89.1	96.3	88.3	89.3	84.0
C16	101.7	94.4	101.3	100.6	95.6	97.9	91.4	97.0	80.6
C17	88.6	84.3	90.8	85.3	88.5	90.1	89.5	93.7	91.9
C18	86.0	88.6	90.8	90.8	85.3	91.4	102.2	114.3	118.8
C19	89.8	89.7	92.9	84.3	90.7	95.2	99.0	101.3	105.4
C21	99.7	98.5	97.1	93.7	99.7	99.4	99.4	106.4	104.5
C22	104.8	102.8	104.3	99.1	100.7	107.8	112.7	109.6	113.4
C23	128.0	156.1	124.2	120.7	124.6	128.3	129.8	124.6	124.4
C24	n.a.	100.0	95.2	94.8	92.6	96.4	96.8	102.6	93.8
C25	n.a.	100.0	94.3	84.4	87.6	102.3	92.3	89.9	97.2

Table 3(g). Fuel Oil Aging - Loss of Normal Paraffin
Location: Chesapeake Light Tower
Oil: 200 gallons No. 4 Fuel Oil
Release: 0800 hrs, EST, 4/26/71
Water Temp: 12°C. Air Temp: 62°F.

% Normal	Time After Release (hrs)								
Paraffin	1:00	3:00	4:00	5:00	6:00	7:00	8:00	9:00	10:00	11:00
C11	105.5	49.7	68.1	55.2	74.7	18.0	22.7	n.d.	11.0	n.d.
C12	152.8	89.0	108.0	93.4	105.0	46.8	64.8	28.8	49.5	42.9
C13	141.5	99.9	107.5	103.9	105.9	84.2	93.2	72.7	78.4	70.7
C14	112.6	104.0	105.4	97.8	104.6	87.5	87.5	81.7	86.1	76.0
C15	106.0	105.0	106.1	104.8	101.8	99.3	102.1	97.5	101.3	92.2
C16	104.6	99.2	96.0	96.8	95.1	89.0	86.6	86.8	94.9	80.2
C17	100.5	101.5	100.4	103.8	98.0	97.0	98.4	96.6	100.3	95.0
C18	104.4	101.3	98.4	98.2	95.6	91.0	92.5	92.2	100.0	89.2
C19	100.8	100.3	99.6	101.2	95.3	95.3	96.8	98.2	100.2	95.1
C21	99.9	99.9	95.3	95.7	97.1	84.7	96.6	93.1	96.8	98.3
C22	112.9	113.5	107.2	109.0	111.4	112.5	115.0	110.6	109.5	111.5
C23	95.8	98.4	87.3	89.9	96.7	97.2	102.4	96.6	95.5	96.0
C24	103.2	111.2	103.4	90.5	99.1	102.3	99.5	95.0	93.9	106.0
C25	99.7	98.1	89.3	84.5	91.5	90.1	94.5	85.7	88.7	94.2

Table 3(h). Fuel Oil Aging - Loss of Normal Paraffin

Location: Chesapeake Light Tower *Avg. of two analyses.
Oil: 200 gallons No. 4 Fuel Oil
Release: 0830 hrs, DST, 8/3/71
Water Temp: 25.5°C. Air Temp:

% Normal	Time After Release (hrs)						
Paraffin	1:00	2:00	3:30	4:45	6:00	6:45	9:00
C10	75.7	53.6	9.4	13.1	3.8	n.d.	n.d.
C11	89.7	77.7	50.3	46.1	34.0	5.0	n.d.
C12	96.1	84.1	64.0	65.3	50.4	46.6	32.8
C13	109.3	108.5	101.2	90.2	83.6	75.9	71.2
C14	84.4	89.5	83.5	89.5	79.5	80.8	74.1
C15	92.4	96.9	95.8	95.8	92.4	92.3	87.8
C16	95.7	99.7	99.9	99.6	96.3	98.5	95.3
C17	95.5	92.2	96.6	96.9	95.0	96.6	92.8
C18	98.0	98.6	98.7	96.1	94.7	98.6	94.7
C19	96.1	100.5	100.4	99.6	99.7	98.9	95.6
C21	103.0	100.5	100.7	98.7	101.8	100.0	98.5
C22	101.8	103.4	99.8	98.4	101.4	99.3	97.1
C23	101.2	96.8	89.0	97.6	99.7	98.7	96.0
C24	98.5	94.8	95.8	96.5	98.9	100.0	93.7
C25	100.5	96.9	100.8	93.9	102.5	100.9	98.6

Table 3(h). (Cont'd). Fuel Oil Aging - Loss of Normal Paraffin

Location: Chesapeake Light Tower
Oil: 200 gallons No. 4 Fuel Oil
Release: 0830 hrs, DST, 8/3/71
Water Temp: 25.5°C. Air Temp:

*Avg. of two analyses

% Normal Paraffin	Time After Release (hrs) 10:00	11:00	25:00	27:30	28:45
C10	n.d.	n.d.	n.d.	n.d.	n.d.
C11	n.d.	n.d.	n.d.	n.d.	n.d.
C12	21.9	13.7	n.d.	n.d.	n.d.
C13	28.9	24.8	3.8	2.4	1.4
C14	65.9	68.4	21.8	15.8	14.5
C15	87.3	86.8	58.9	52.1	42.0
C16	96.4	92.6	83.8	81.2	75.8
C17	93.5	91.7	86.7	85.9	82.9
C18	94.8	92.8	91.8	92.6	92.6
C19	97.6	96.9	95.0	96.7	94.4
C21	99.0	103.6	101.2	97.8	98.9
C22	96.5	104.5	100.3	96.9	98.7
C23	95.8	102.8	100.4	95.6	95.0
C24	95.2	104.7	100.4	97.4	96.7
C25	99.1	103.5	100.6	96.1	98.2

Table 3(i). Fuel Oil Aging - Loss of Normal Paraffin
Location: Chesapeake Light Tower
Oil: 200 gallons No. 2 Fuel Oil
Release: 0730 hrs, EST, 1/20/71
Water Temp: 5°C. Air Temp: 40°F.

% Normal Paraffin	Time After Release (hrs) 1:00	3:00	5:00
C10	28.5	17.1	n.d.
C11	76.5	73.6	13.4
C12	92.8	92.2	44.7
C13	93.4	n.a.	63.1
C14	103.1	n.a.	107.8
C15	86.7	n.a.	95.9
C16	99.9	n.a.	112.9
C17	99.2	101.9	114.2
C18	111.9	114.1	126.9
C19	99.0	100.1	111.2
C21	100.6	100.0	109.4
C22	79.9	86.7	103.1

Table 3(j). Fuel Oil Aging - Loss of Normal Paraffin
Location: Mobjack Bay
Oil: 200 gallons No. 2 Fuel Oil
Release: 0845 hrs, EST, 3/16/71
Water Temp: 8.3°C. Air Temp: 40°F.

% Normal Paraffin	Time After Release (hrs) 0:20	0:50	1:25	1:45	2:00	3:00	3:25	3:40	5:25
C9	91.1	19.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
C10	96.7	74.7	23.6	3.8	8.3	n.d.	n.d.	n.d.	n.d.
C11	112.0	118.5	56.4	13.1	7.2	n.d.	n.d.	n.d.	n.d.
C12	107.6	126.2	50.0	23.4	17.0	n.d.	n.d.	n.d.	n.d.
C13	101.3	127.3	104.2	59.2	50.1	4.3	2.9	n.d.	n.d.
C14	119.8	140.5	130.8	100.8	114.6	37.5	11.3	n.d.	n.d.
C15	116.6	139.6	124.0	112.5	120.8	75.2	44.9	n.d.	n.d.
C16	113.0	139.0	118.5	121.3	125.0	99.3	98.7	18.1	0.9
C17	115.3	134.6	139.2	139.8	152.8	131.9	137.3	85.8	23.6
C18	111.8	129.7	118.8	121.6	131.8	121.0	127.7	154.0	88.5
C19	107.7	115.8	120.4	122.5	132.5	121.5	145.5	151.3	113.1
C21	98.2	90.4	103.1	89.0	82.7	85.7	84.7	141.2	117.8
C22	101.2	92.5	85.4	87.2	77.8	79.7	78.6	84.7	85.8

Table 3(k). Fuel Oil Aging - Loss of Normal Paraffin
Location: Chesapeake Light Tower
Oil: 200 gallons No. 2 Fuel Oil
Release: 0900 hrs, DST, 8/30/71
Water Temp: 23°C. Air Temp: 76°F.

% Normal Paraffin	Time After Release (hrs)						
	1:30	3:20	4:45	5:45	6:45	7:40	10:30
C10	42.3	36.4	8.0	18.6	n.d.	4.3	n.d.
C11	68.6	69.8	28.6	55.9	7.0	27.9	20.9
C12	74.9	73.5	43.8	61.7	12.6	34.7	31.5
C13	84.9	86.5	72.8	83.5	41.1	64.4	74.6
C14	88.2	91.5	87.7	90.9	72.4	81.4	94.9
C15	87.6	92.6	88.9	90.5	80.1	85.2	110.5
C16	91.5	97.3	98.5	95.6	91.6	93.3	124.1
C17	91.9	96.7	95.4	93.6	83.7	86.7	109.3
C18	95.9	98.3	97.2	98.1	92.3	91.7	113.4
C19	95.3	96.6	96.6	94.0	90.6	90.1	106.0
C21	93.1	95.7	86.2	80.5	90.6	96.5	80.5
C22	103.6	90.6	103.6	80.5	97.2	96.8	80.5

Table 3(1). **Fuel Oil Aging - Loss of Normal Paraffin**
Location: Chesapeake Light Tower
Oil: 200 gallons No. 2 Fuel Oil
Release: 1045 hrs, DST, 10/13/71
Water Temp: Air Temp:

% Normal Paraffin	1:00	2:09	4:30	5:30	6:30
C10	83.0	28.6	8.3	n.d.	n.d.
C11	101.4	70.3	54.9	28.8	30.2
C12	105.9	97.7	103.1	77.7	69.6
C13	109.5	109.0	121.8	94.8	92.1
C14	106.4	106.8	123.0	103.4	99.9
C15	107.4	108.6	127.0	107.5	104.9
C16	106.5	110.1	128.7	106.3	107.5
C17	107.4	111.0	128.2	107.4	106.9
C18	104.0	108.8	123.7	106.7	105.5
C19	106.6	110.1	119.7	109.4	105.5
C21	93.3	89.7	0.765	90.3	93.6
C22	98.3	67.5	0.572	81.3	93.5

The loss of oil components from an oil film is a complex problem to treat mathematically. A simple model is considered here, as a basis for comparison with the aging study. The model system chosen is an oil film of fixed volume and surface area which is losing components by evaporation to an air stream passing over it. Preliminary assumptions are made that the heat input is sufficient to maintain the oil film at constant temperature, and that the oil components are in continuous equilibrium with a finite air volume above the film. A further assumption is that the total number of moles of all compounds in the oil film is not appreciably changed by the evaporative loss of volatile compounds.

Define:

C^t = number of moles of component C in the oil at time t.
K = Henry's Law constant.
M = Total number of moles of all components in the oil.
F = flow rate of the air stream.
V = volume of air in equilibrium with the oil.
P_c^t = partial pressure of C in V at time t.

The rate of loss of C from the oil will be given by the amount of C evaporated into V per unit time. Therefore, using the ideal gas law:

$$-\frac{dC}{dt} = \frac{P_c^t V}{RT_t}$$

Henry's Law states that the partial pressure of a component in the vapor phase is directly proportional to the mole fraction of that component in the liquid phase with which the vapor is in equilibrium. Thus:

$$P_c^t = \frac{C^t K}{M}$$

and since V = Ft, the equation becomes:

$$-\frac{dC}{Dt} = \frac{KFC}{MRT}$$

Integrating from t = 0 to t = t ,

$$-\frac{KFt}{MRT} = \ln C^t - \ln C^o$$

Or, $\ln(\frac{C^t}{C^o}) = -\frac{KFt}{MRT}$

And the $\ln(\%C)_t$, that is, the log percent C remaining at time t, will be a linear function of t:

$$\ln(\%C)_t = -\frac{KFt}{MRT} + \ln(100)$$

For aging experiments in the field, then one might expect, to a first approximation, that linear relationships between log $(\%C_i)_t$ vs time would be obtained. Data of several n-paraffin analyses from one of the field experiments are shown plotted in the above manner (Figure 14). These plots of log $(\%C_i)_t$ vs t are not linear, but curve downward. This non-linearity may have resulted from a number of causes:

1.) The temperatures of the oil films and air are not constant.

2.) The wind speed in the field is not constant.

3.) Neither the surface area nor the thickness of the oil film is constant, because of the spreading tendency of unconfined oil on the sea surface.

The temperature of the oil film is not explicit in the model equation of oil aging, but the Henry's Law proportionality constant is an exponential function of temperature. The gigher the temperature of the oil film, the larger the value of K becomes. The effect of increasing wind speed will be to increase the magnitude of the factor F, but the relation may not be a linear one at high wind speeds. Finally, there is the problem of changing surface area and thickness of the oil film. Although the assumption was made that the oil components are in continuous equilibrium with the passing air volume, this situation will be approached only at low wind speeds and very thin film thickness. The effect of oil spreading, then, will be to increase the magnitude of the factor KF.

The effect of increased temperature, wind speed, and surface area, then, is to increase the magnitude of the slope coefficient $-\frac{KF}{MRT}$, and to increase the rate at which C_i is lost from the oil film.

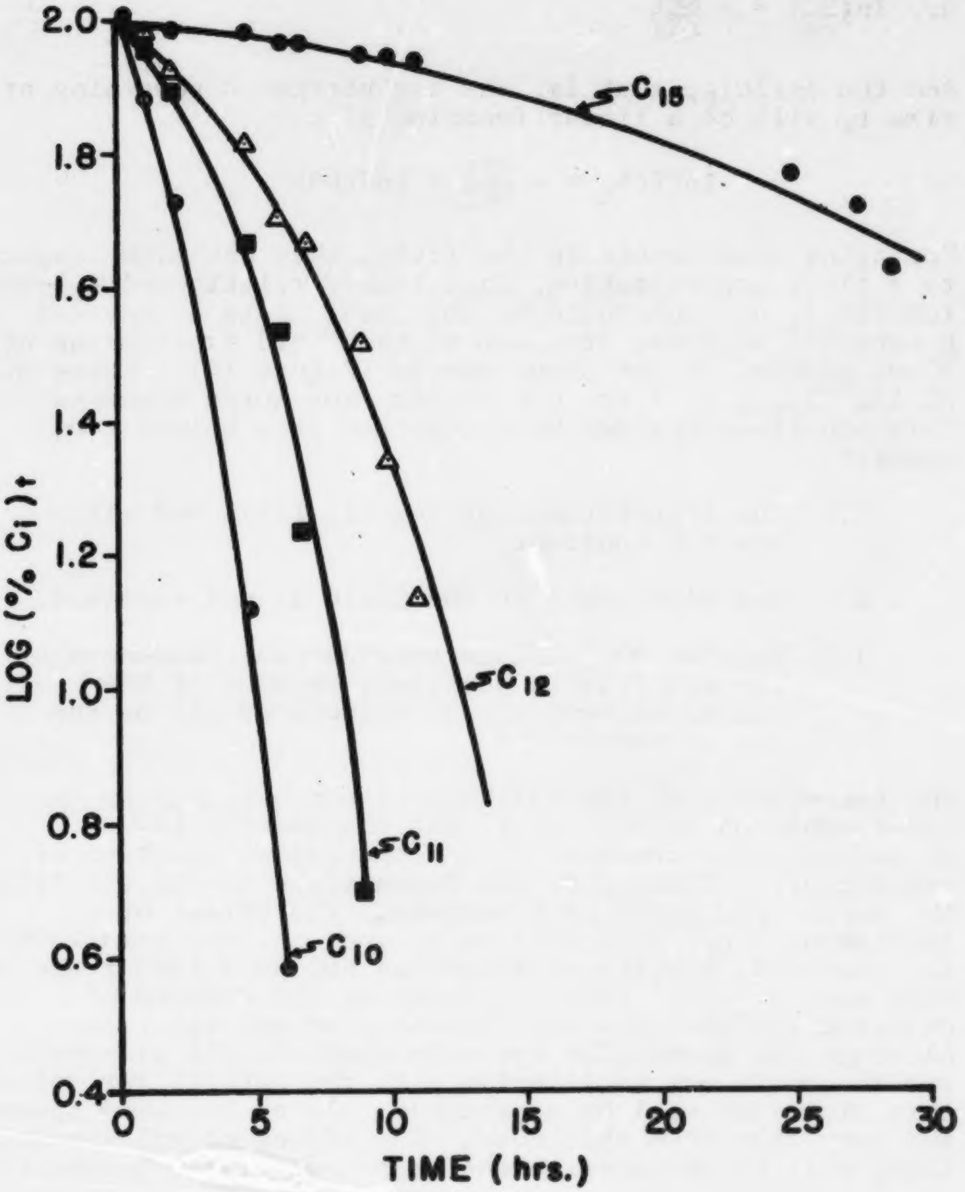

Fig. 14. Loss of n-paraffins from No. 4 fuel oil release, Aug. 3, 1971.

In the field releases, which were generally initiated in the cool, still, early morning, the usual conditions experienced were increasing temperature, wind speed, and surface area. Thus, plots of log $(\%C_i)_t$ show increasing curvature as a function of time.

Laboratory aging of the three fuel oil types in the bubbler aging apparatus was conducted to get information on the relative importance of loss of oil components by evaporation and by dissolution in seawater. The amount of material from the oil film which was dissolved in the seawater after a period of aging was determined by quantitative gas chromatography of pentane extracts of the seawater. This information is listed in Table 4. The extracts of the seawater which was in contact with the three oil types produced qualitatively similar gas chromatograms of the aromatic portions of the oils. Figure 15 compares the chromatogram of the seawater extract from the No. 4 fuel oil aging experiment with the aromatic portion of the No. 4 fuel oil distillate fraction, b.p. 190-250°C/760 torr.

Table 4. Dissolved oil components from bubbler experiment.

Fuel Oil	Concentration of oil components	Percentage of total oil
No. 2	1.425×10^{-3} g/l	0.048%
No. 4	7.47×10^{-4} g/l	0.025%
No. 6	1.26×10^{-4} g/l	0.004%

The major water-soluble components from all three oil types were naphthalene and the isomeric monomethyl- and dimethylnaphthalenes. The naphthalene and monomethylnaphthalene peaks were identified from their mass spectra, and by comparison of their gas chromatographic retention times with those of authentic samples. The identity of the isomeric dimethylnaphthalenes was inferred from their retention times relative to that of naphthalene and the monomethylnaphthalene, with reference to reported gas chromatograms (Boylan & Tripp, 1971).

The differences noted in the weights of dissolved oil compounds among the three oil types is probably related to concentrations of water-soluble aromatic compounds in the original oil. The No. 2 fuel oil contains the highest

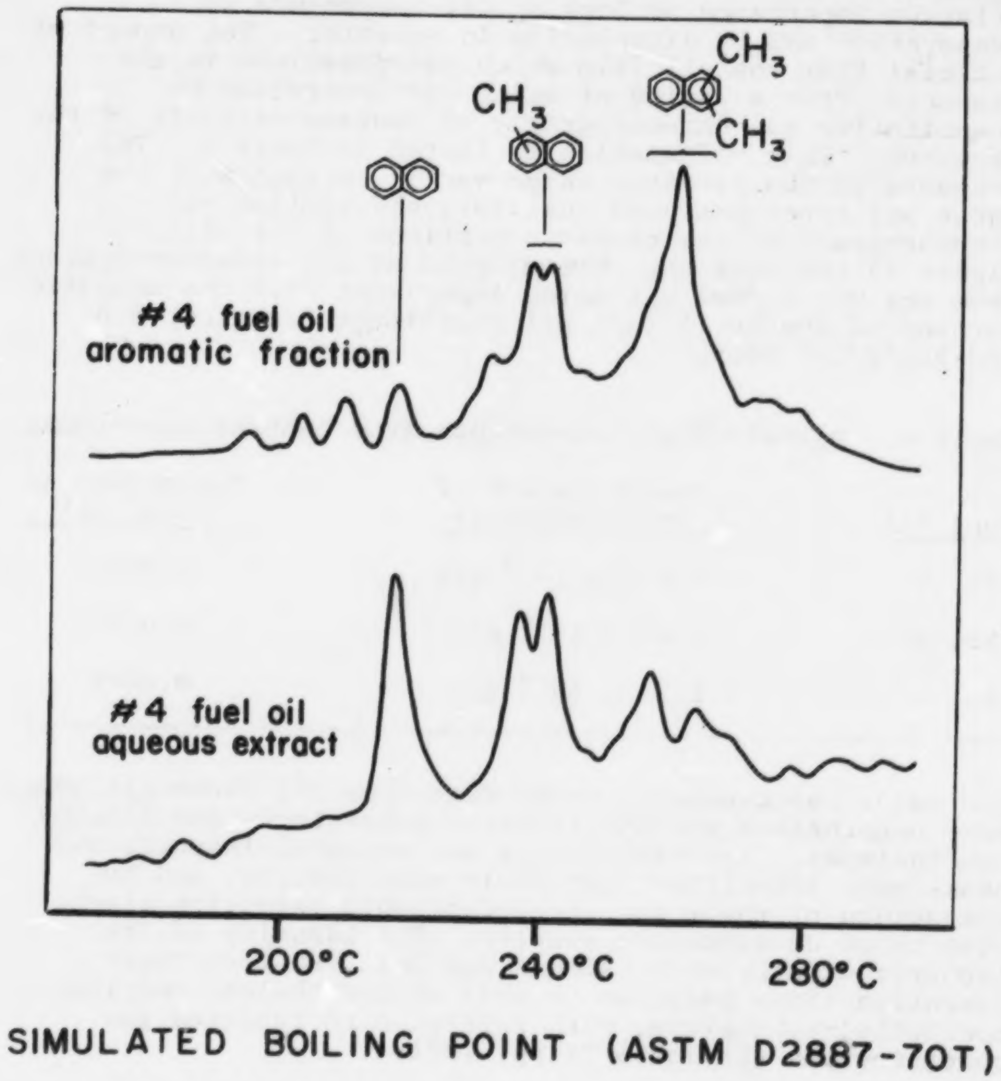

Fig. 15. Comparison of No. 4 fuel oil aromatic fraction b.p. 190°-250°C with No. 4 fuel oil water solubles.

naphthalenes found (218-262°C), whereas No. 4 and No. 6 fuel oils contain respectively less.

Several interesting features were noted of the character of the seawater extracts from the bubbler aging experiments. One is the relatively low concentration of naphthalene in the seawater. In all three experiments, the concentration of naphthalene was one to two orders of magnitude lower than the maximum calculated solubility of naphthalene in a 33‰ aqueous sodium chloride solution, 1.9 x 10^{-2}g/l (Gordon and Thorne, 1967). The other is the noticeable absence of the lower boiling, rather water-soluble alkyl-benzenes. Boylan & Tripp (1970) found considerable quantities of these species in seawater which had been equilibrated with various types of fuel oils and crude oils in closed systems. It is postulated that in the bubbler apparatus, and also in open water oil spills, the volatile water soluble aromatic compounds are lost preferentially by evaporation. The evaporative loss might be occurring directly from the oil film, or could come from the scrubbing of the seawater by the bubbler, or wave action.

The possibility that dissolved aromatic compounds could be scrubbed out of seawater solution by interaction with the air was demonstrated in a quantitative manner. A solution of cumene (isopropyl benzene, b.p. 152°C), naphthalene (b.p. 218°C), and 1-methylnaphthalene (b.p. 241°C) was allowed to age in the bubbler apparatus. The content of these species in the seawater was determined by gas chromatographic analysis of the pentane extracts of the seawater as a function of time. Figure 16 shows the plot of log (% remaining) vs time for the three species. The scrubbing action of the bubbler followed an exponential decay, and produced straight line plot. The lowest boiling component, cumene, was lost beyond detectability by the process in less than four hours. The naphthalene and 1-methylnaphthalene were lost at slower, though appreciable rates.

Therefore, in the bubbler experiments, and presumably in the oil releases at sea as well, the lower boiling aromatic compounds, though rather soluble in seawater, are lost through an evaporative process, either directly, or by scrubbing of the water column, leaving the less volatile, higher molecular weight aromatics as the major dissolved species. Since solubility in water of aromatic compounds generally decreases as the molecular weight and size of the compound increases, it seems that the naphthalene, monomethylnaphthalenes, and dimethylnaphthalenes occupy a prominent position of favorable compromise between the

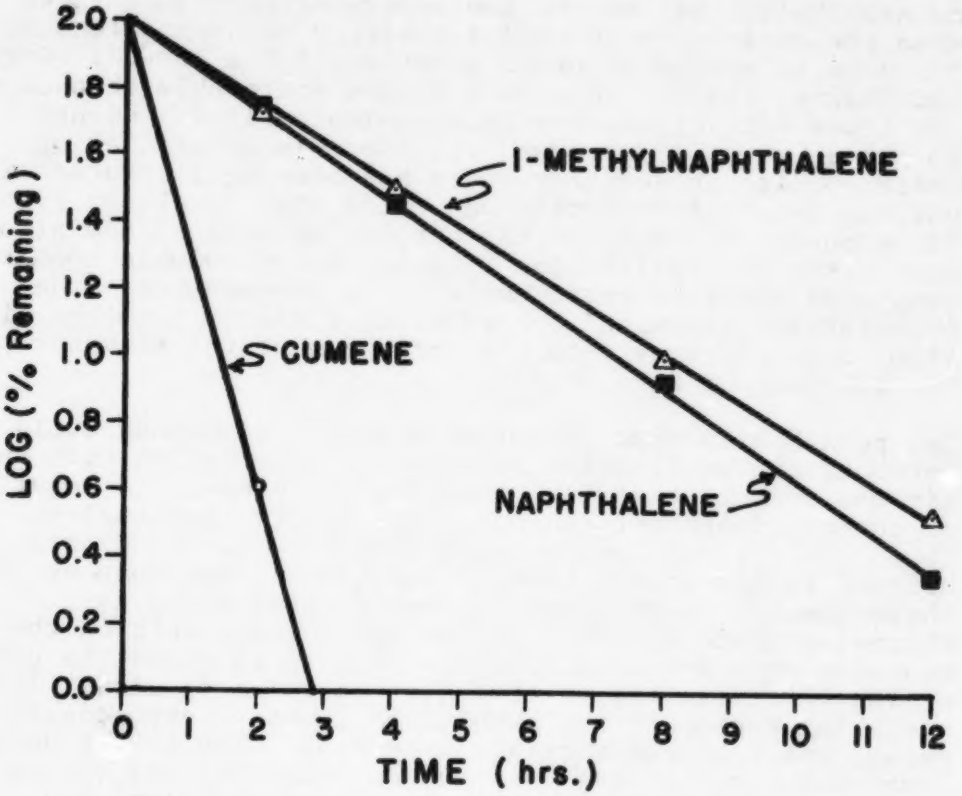

Fig. 16. Scrubbing of dissolved aromatic species in bubbler apparatus.

opposing characteristics of volatility and solubility in seawater.

The boiling ranges of the trapped evaporate fractions from the bubbler apparatus for the three oil types were determined by ASTM D2887-70T Boiling Range Test by Gas Chromatography. Figure 17 shows the changes in the initial and final boiling points with time. The results from all three oil types were similar, so that single lines were drawn to fit points from the three experiments. The final boiling point of the fraction levels off in the vicinity of 270°C, while the initial boiling point continues to increase. Presumably, the lines will eventually converge. Because of this behavior, the term volatile fraction is introduced to describe that fraction of the fuel oil which has a boiling point of 271°C or less. The boiling range of the volatile fraction was defined to include n-pentadecane, b.p. 271°C as its upper limit, as this compound was detected in the evaporate fraction.

Although the boiling ranges of the evaporate fraction is similar for the three oil types, the detailed nature of their components is not. Figure 18 compares the gas chromatogram of the evaporate fractions from the three oil types at comparable aging times. It should be noted that the three were recorded at different relative amplifications, however. The horizontal axis is in units of simulated boiling point, derived from ASTM D2887-70T instead of the more usual retention time.

The loss of the components from the oil is shown in Figure 19. The loss of weight is greatest for No. 2 fuel oil, and respectively less for No. 4 and No. 6 fuel oils. This result is no doubt related to the relative sizes of the volatile fractions, i.e., b.p. $\leq$ 271°C, in the three oils.

Although the derivation for model aging which was treated above considered the loss of a single compound, its main point, that the aging process should be an exponential function of time, may be applied here. If the volatile fraction is treated as a single entity rather than a variety of compounds, one can plot log (% volatile fraction remaining) vs time instead of $(\%C_i)_t$. Such a plot is shown in Figure 20. Here, the loss of the volatile fraction is not quite linear with respect to time, and shows curvatures, particularly in the early hours of aging. This presumably is due to the loss of the extremely volatile compounds. The slopes of No. 4 and No. 6 fuel oils become quite similar, though that of No. 2 fuel oil is larger, reflecting its

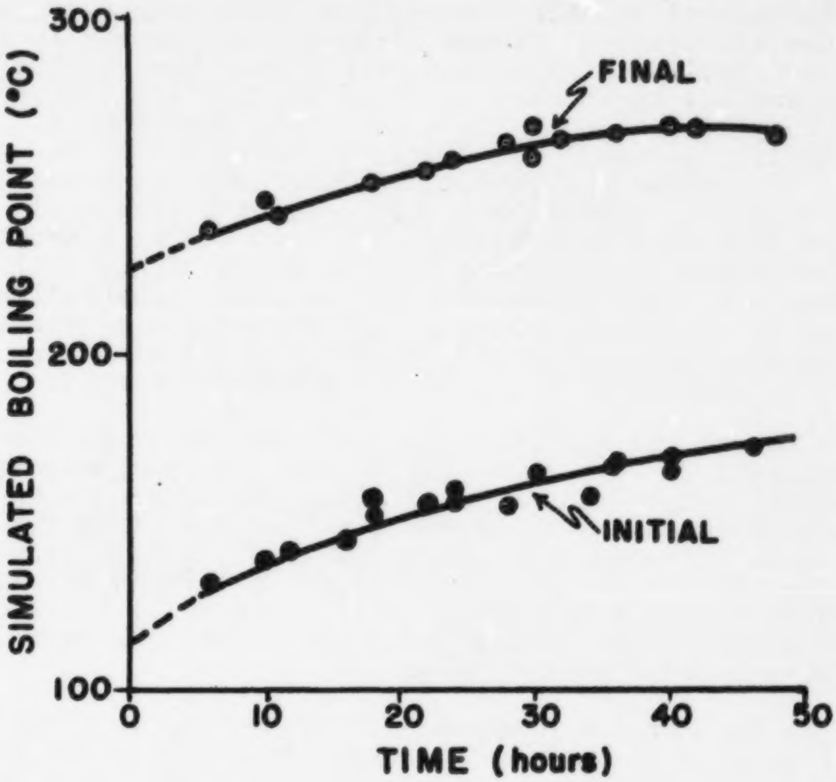

Fig. 17. Change in boiling range of evaporate fraction in bubbler apparatus.

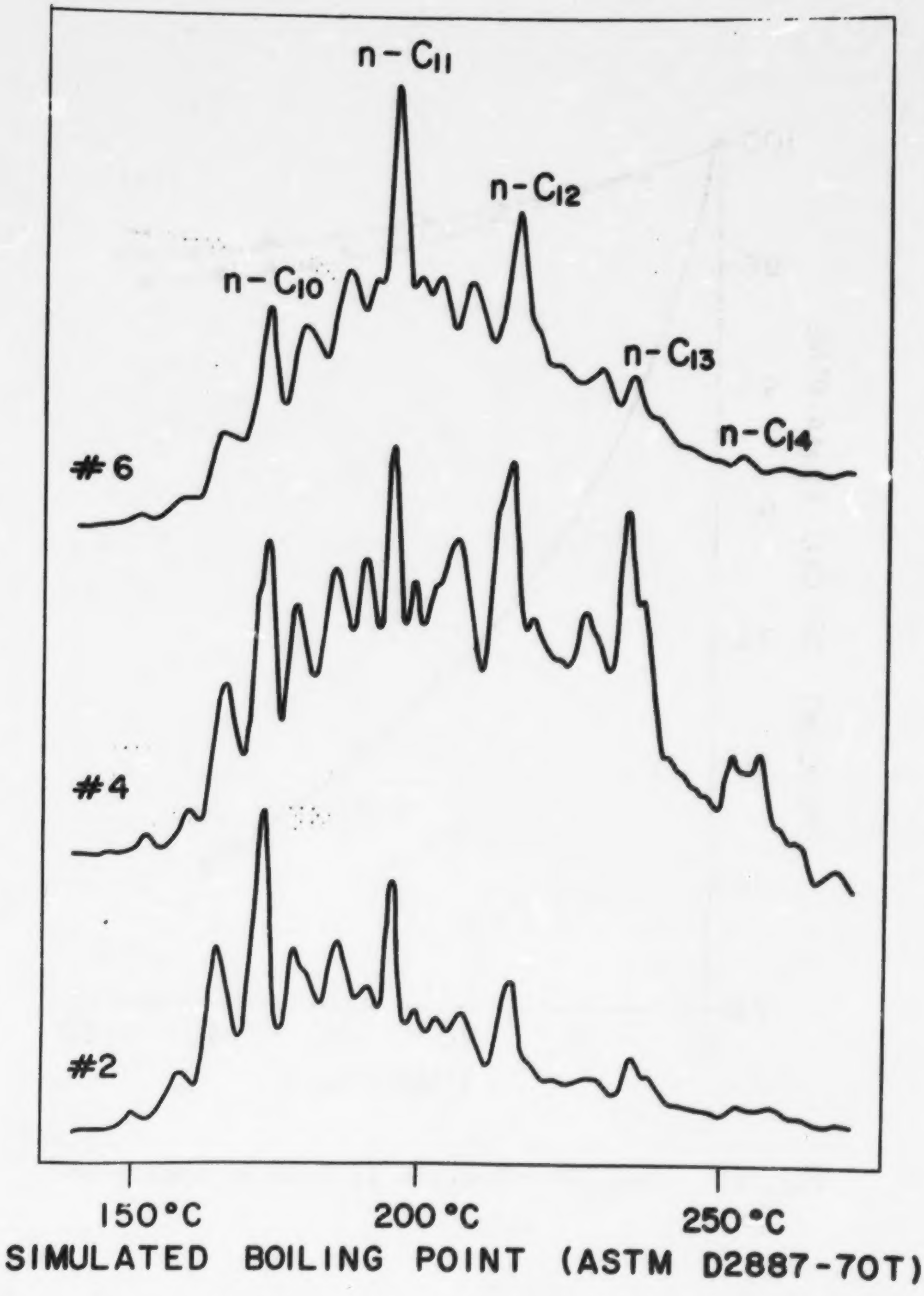

Fig. 18. Typical gas chromatograms of No. 2, 4, and 6 fuel oil evaporate fractions.

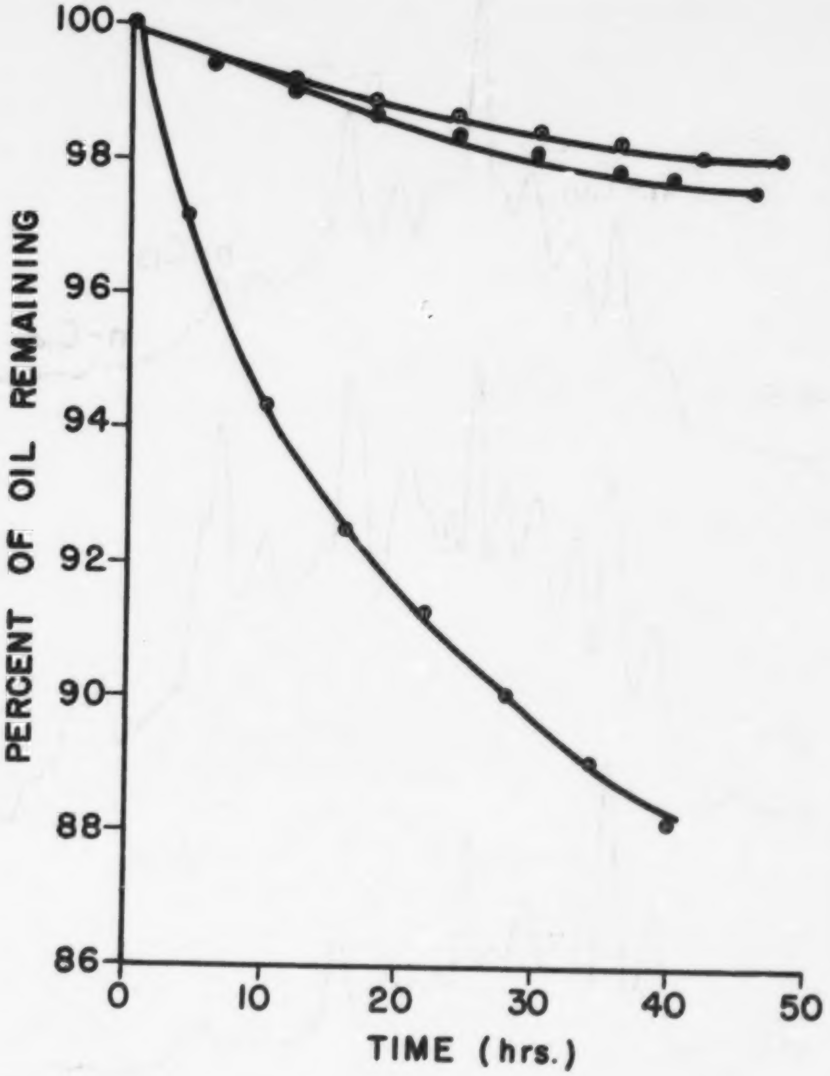

Fig. 19. Loss of volatiles in bubbler apparatus.

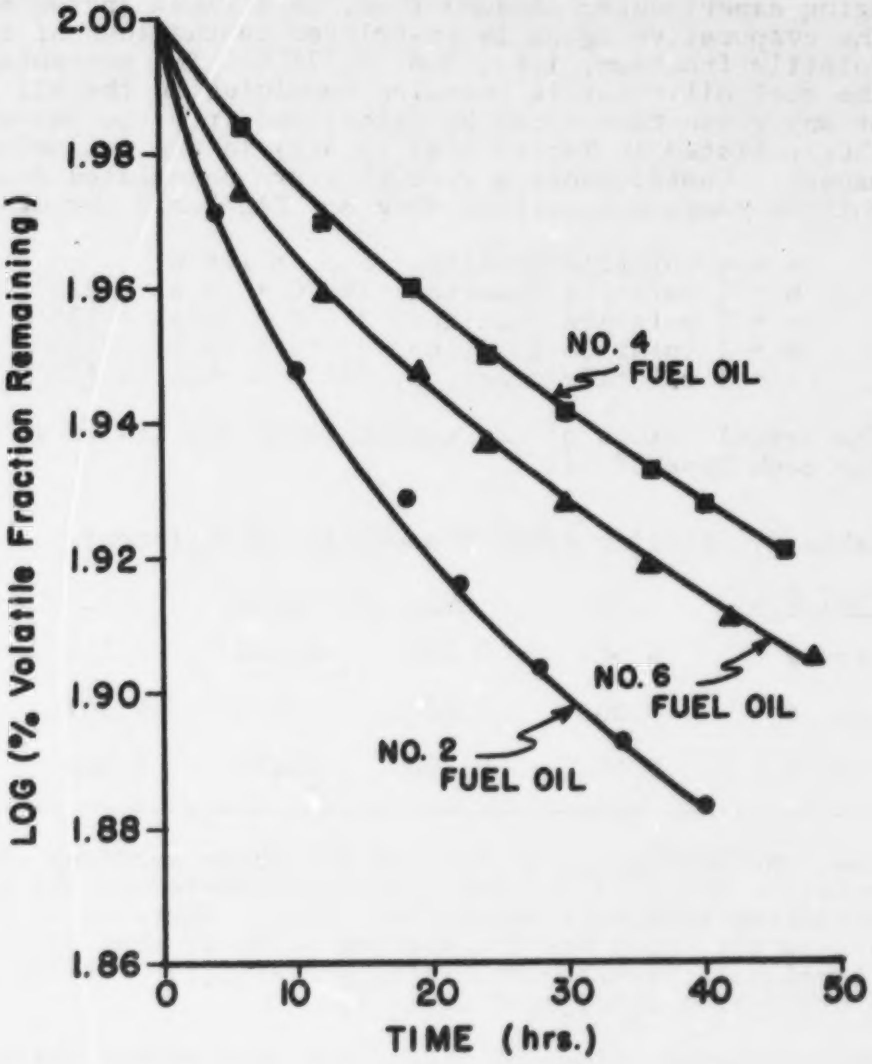

Fig. 20. Volatiles remaining in bubbler apparatus.

greater content of more volatile compounds.

A scheme has been devised to allow comparison of the aging of fuel oils in the bubbler apparatus with the open ocean aging experiments. Assume that, to a first approximation, the evaporative aging is restricted to the loss of the volatile fraction, i.e., b.p. ≤ 271°C. The percentage of the fuel oil volatile fraction remaining in the oil film at any given time t can be calculated from the values of $(\%C_i)_t$ listed in Tables 3(a) to 3(l) in the following manner. Coefficients a through e are calculated from the boiling range composition diagram, Figures 9 through 11:

a = % volatile fraction, b.p. ≤ 196°C
b = % volatile fraction, 196°C < b.p. ≤ 216°C
c = % volatile fraction, 216°C < b.p. ≤ 235°C
d = % volatile fraction, 235°C < b.p. ≤ 253°C
e = % volatile fraction, 253°C < b.p. ≤ 271°C

The actual values of the coefficients are listed in Table 5 for each type of oil.

Table 5. Boiling Range Composition Coefficient

Fuel Oil	a	b	c	d	e
No. 2	0.080	0.140	0.230	0.310	0.240
No. 4	0.000	0.067	0.233	0.367	0.333
No. 6	0.000	0.300	0.250	0.200	0.250

Now, the percentage in each of the above portions of the volatile fraction at time t is approximated by the gas chromatographically determined $(\%C_i)_t$, where C_i is the n-paraffin which has its boiling point in that portion: $(\%\ \text{volatile fraction remaining})_t = a(\%C_{11})_t + b(\%C_{12})_t + c(\%C_{13})_t + d(\%C_{14})_t + e(\%C_{15})_t$.

The tabulated values of $(\%C_i)_t$ are used except where $\%C_i > 100\%$, in which case the value is assumed to be 100%. The resulting data are plotted in the usual manner as log (% volatile fraction) vs time. The plots from each oil release, along with the corresponding bubbler aging plot are shown in Figures 21 through 23. The slope of the visually fitted straight line through the points for each experiment was determined and recorded in Table 6. The values of the slopes gives a rough estimate of relative aging. When correlated in this manner, the open water oil films aged consistently faster than the bubbler films, ranging from 2-180 times as fast.

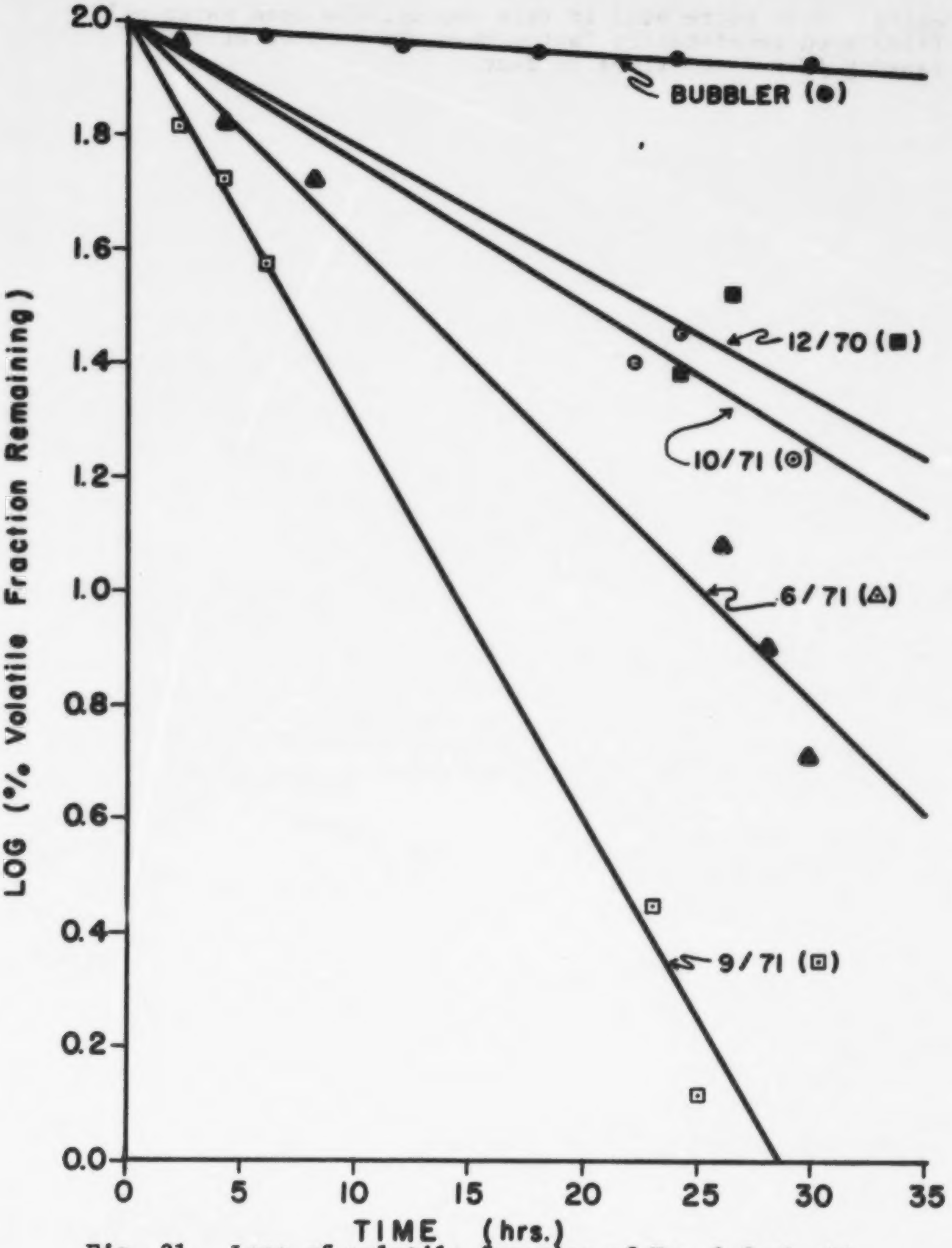

Fig. 21. Loss of volatile fraction of No. 6 fuel oil in bubbler and field experiments.

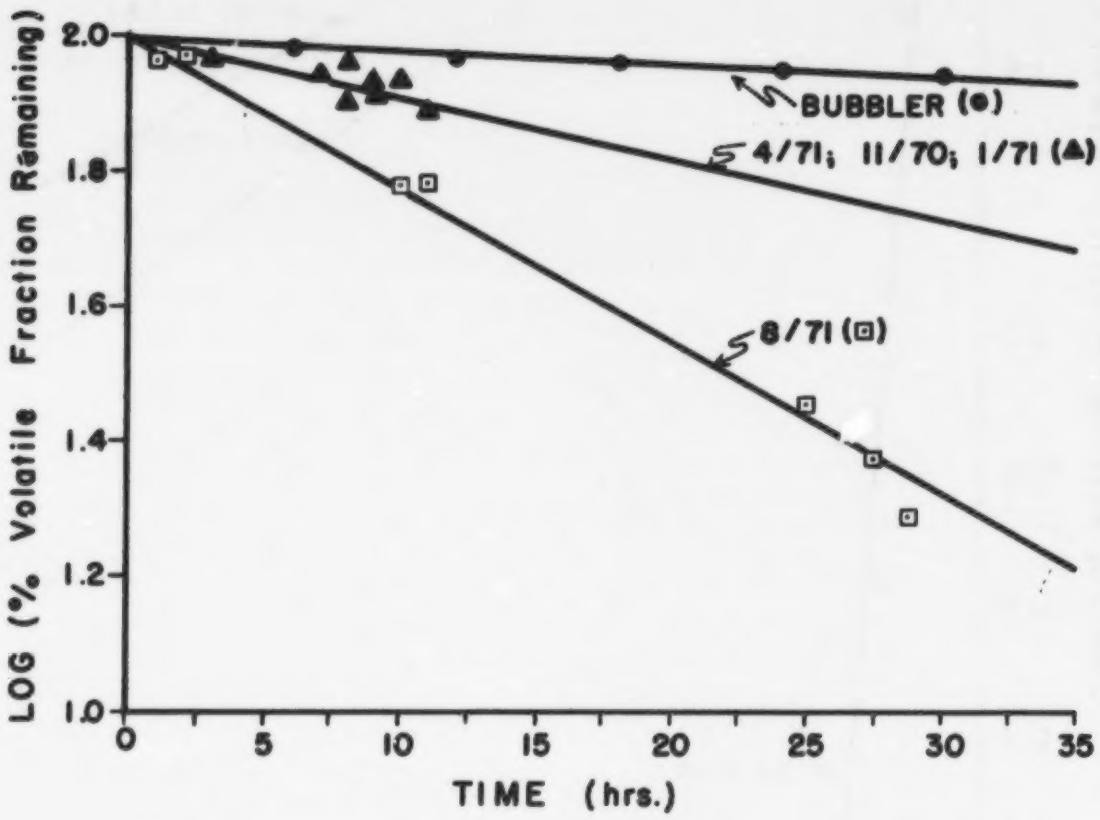

Fig. 22. Loss of volatile fraction of No. 4 fuel oil in bubbler and field experiments.

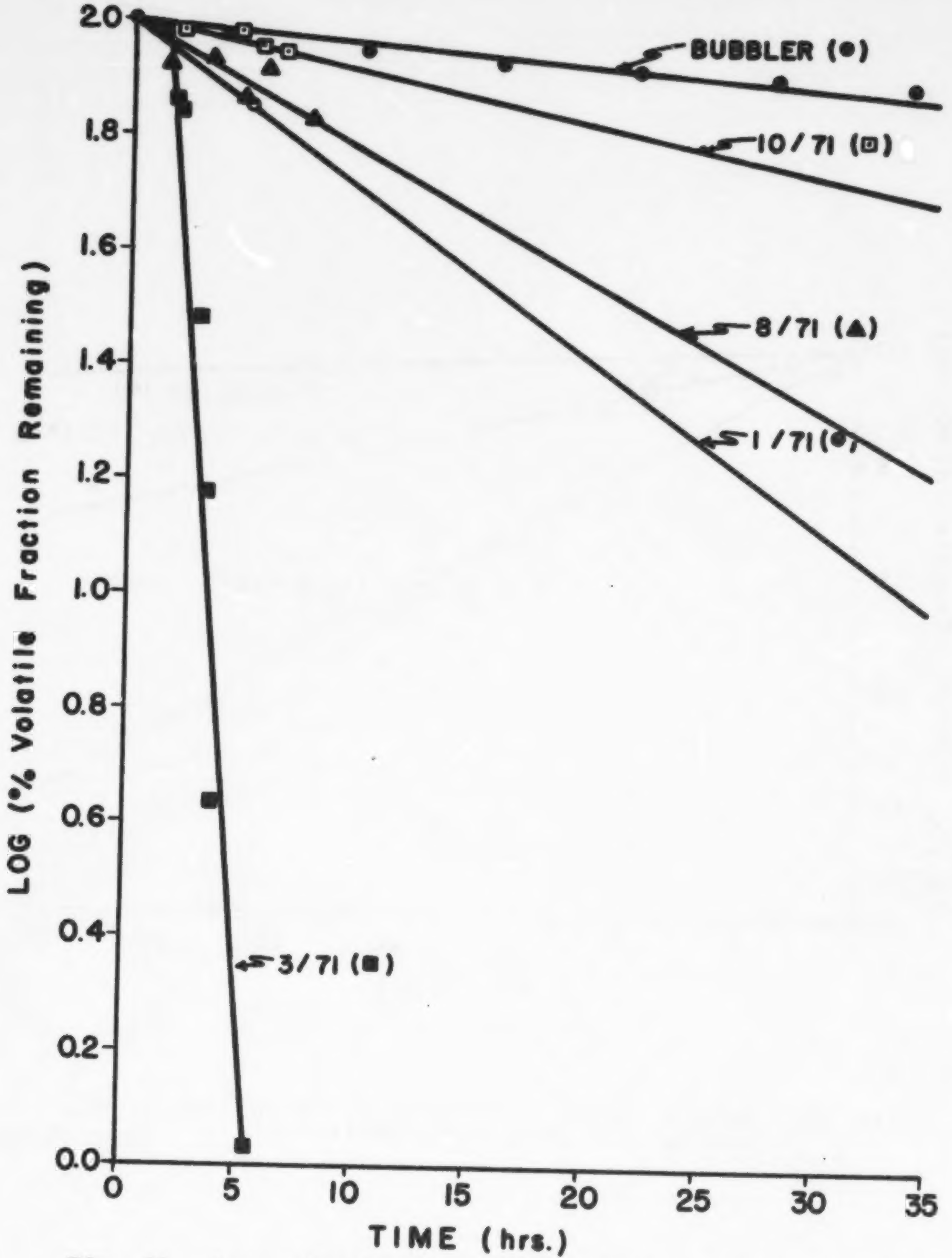

Fig. 23. Loss of volatile fraction of No. 2 fuel oil in bubbler and field experiments.

Table 6. Fuel Oil Aging Comparison.

Experiment	Slope log (% remaining) Units/hr	Aging Rate Relative to Bubbler
No. 2 Fuel Oil		
Bubbler	2.94×10^{-3}	1.00
1/71 Release	2.45×10^{-2}	8.33
3/71 Release	5.28×10^{-1}	179.59
8/71 Release	2.09×10^{-2}	7.11
10/71 Release	6.67×10^{-3}	2.27
No. 4 Fuel Oil		
Bubbler	1.96×10^{-3}	1.00
11/70 Release	7.02×10^{-3}	3.58
1/71 Release	7.02×10^{-3}	3.58
4/71 Release	7.02×10^{-3}	3.58
8/71	2.33×10^{-2}	11.89

Table 6. (Cont'd). Fuel Oil Aging Comparison.

Experiment	Slope log (% remaining) Units/hr	Aging Rate Relative to Bubbler
No. 6 Fuel Oil		
Bubbler	2.27×10^{-3}	1.00
12/70 Release	2.13×10^{-2}	9.38
6/71 Release	3.66×10^{-2}	16.12
9/71 Release	7.66×10^{-2}	33.74
10/71 Release	2.50×10^{-2}	11.01

SECTION VI

REMOTE SENSING OF OIL SLICKS

Oil remote sensing techniques have been applied to the deliberate oil releases, natural films, and accidental oil spills observed in this project. Oil types included menhaden fish oil and numbers 2, 4, and 6 fuel oils.

Overflights of oil slicks have been made by a C-54 and a helicopter provided by NASA Wallops Station. These aircraft were equipped with multiple nadir view 9-in. format Fairchild T-11 cameras. In one experiment, coverage was also provided by the University of Michigan C-47 aircraft, which carried two 70 mm format cameras and two multispectral scanners to collect data in 17 spectral channels.

Remotely sensed and surface collected data have been used to analyze oil slick temperature, thickness, and spreading rate, and to evaluate techniques for remote detection and discrimination of various oils. Accurate surface measurements have made the evaluation of remote sensing data especially reliable. The oil slick remote sensing program is continuing and other observation frequencies and modes are being evaluated. Passive microwave radiometric oil thickness measurements are now being processed by the Naval Research Laboratory, which operates the instrument.

REMOTE SENSING COVERAGE

There were twelve experiments with remote sensing coverage. Film-filter combinations and non-photographic detectors are listed in Table 7, which includes photography of No. 6 oil from an accidental 10,000 gallon spill on May 6, 1971, from the Amoco Refinery at Yorktown, Virginia. Remote sensing records are available at NASA Wallops Station. Surface data are located at the reporting agency.

SURFACE DATA COLLECTION

Surface data was collected from small inflatable boats stationed in the slicks, so observations were generally conducted in fair weather with winds less than 15 knots and wave heights less than one meter. Meteorological data were collected from the oil release vessel. Extent of haze, water color and turbidity, apparent current boundaries, and biological features were noted.

Table 7. Oil Slick Remote Sensing Experiments

Date	Oil Type	Coverage
12 Sept. 69	6	Tri-X/47B Kodachrome II 8443/15
26 Sept. 69	6 and menhaden	8403/47B 8443/1A
27 Oct. 69	6	8403/47B Kodachrome II
12 Aug. 70	2	2405/15 8442/1A 2403/47 8443/15
6 Nov. 70	4	2492/18A 2403/57 2403/47 8443/12 2424/89B SO-397/1A 2443/12 multispectral scanner
3 Dec. 70	6	2403/47 2448/pol. 2448/1A
21 Jan. 71	2	2403/47+pol. 2445 2445/pol. 2443/12 2403/18A
26 Apr. 71	4	2403/47 2403/57 SO-397 2443/12
6 May 71	6	2443/1A 2443/15,20B SO-397/1A
3 Aug. 71	4	SO-397/1A 2443/12 2403/47 2403/57 microwave radiometer infrared scanner

Table 7. (Cont'd.). Oil Slick Remote Sensing Experiments

Date	Oil Type	Coverage
30 Aug. 71	2	microwave radiometer 2443/1A SO-397/1A 2403/57 2403/47
4 Sept. 71	6	2443/1A 2403/47 2403/
13 Oct. 71	2 and 6	microwave radiometer

A floating thermistor device was used to measure water surface and oil slick temperatures. The thermistor (L type, 5000 Ω at 25 C, Applied Research Austin, Inc., Austin, Texas) was attached to the end of a spinal tap needle mounted with vertical adjustment in a triangle frame of stainless steel rod. Flotation of the frame was provided by a ping-pong ball glued to each apex. The design was similar to Marlatt's (1967), but did not damp capillary waves, and should indicate more closely the undisturbed surface temperature. A fishing pole was used to place the device at least one meter away from the boat hull, and carried the wires leading from the thermistor to the temperature readout unit. The thermistor was calibrated against a mercury stem thermometer, using the freezing point of distilled water as a reference. This technique measured temperature in the upper 2 mm of the surface layer. Subsurface temperatures with the unit were compared occasionally with those taken by stem thermometer.

Oil film thickness was calculated from the volume collected in a 10 ml graduated pipette blown to the stem of a glass funnel. The funnel, when pushed through the slick, acted as a thickness amplifier, and was calibrated over the thickness range 0.5-2.5 mm with No. 2 oil. Other funnel pipettes were calibrated down to 30 μm thickness. The funnels were limited to use in calm water, produced erratic field data despite good prevision in the laboratory, and worked poorly with No. 6 oil which adhered to glass surface even when they were precoated with photo-flow solution. More accurate thickness data for heavy oils can be obtained by weighing retrieved film samples, or by solvent extracting them for colorimetric analysis. For thickness less than 50 μm, appearance was converted to thickness using the graph of Allen (1969), or Allen and Schleuter (1969).

Each oil type used had its own visual characteristics, which are described in the following paragraphs. In general, these characteristics were present in aerial color photographs, but much of the fine detail was lost, for example, the distinction between No. 4 from No. 6 fuel oil was lost.

Number 2 fuel oil spread rapidly. The slicks were thin and symmetrical with interference rings near the edge, and a large lens area in the center with an obvious yellow color. This lens was broken only by vigorous wave action. Aggregation into lumps or fibrils was never observed.

Number 4 fuel oil spread more slowly, and the resulting slicks were much less regular in shape. Interference colors were present around the slick edge and between areas where there were lenses of thicker oil. These thin regions were compressed by wave action and formed thin brown fibrils of oil that mixed below the water surface and spread again when the forces leading to their compression were removed. The lenses were visually thicker than with No. 2 oil and were very dark brown. These slicks did not fragment and clump.

Number 6 fuel oil was not observed to spread after initial hydrodynamic energies of introducing the oil were dissipated. The interference portions of the slick were much smaller in area than for the other two fuel oils. The lens portions of slick were difficult to disturb and appeared like a crinkled warm asphalt when waves passed under them. Lens were of irregular shape and their number and extent depended on the manner of introduction of the oil. Number 6 oil had a high coherence with itself, but, when the lens were broken by breaking waves, small fragments of oil did not reform the lens structure. The oil mixed down into the water column as irregular fragments, with the tendency to fragment increasing in experiments conducted at lower water temperatures.

The appearance of these oils should vary with the source, but the physical characteristics, such as viscosity, pour point and other properties of the fuel oil types are sufficiently different to allow visual distinction on water. This situation might be changed as the oil ages, but the oils generally dissipated before obvious changes occurred in these small releases. The only aging change was that No. 6 fuel oil aged over 1 day at sea was present in fragments with much less thin oil and interference rings than was present immediately following release.

REMOTE SENSING ANALYSIS

Photographic film was developed by the laboratory at NASA Wallops Station and their contractors. Images were not rectified for aircraft attitude. Multispectral scanner data were reduced at the Willow Run Laboratories of the University of Michigan. Data from all channels were processed to a continuous-tone photographic format. Ultraviolet and thermal infrared signals were processed by voltage-slicing to give a radiance-contoured photographic format. The contour intervals were assigned ranges of equivalent black body temperature based on scanner readings of two thermostated black body reference plates (Hasell and Larsen, 1968).

INFRARED SCANNER CALIBRATION

Infrared scanner temperatures from the oil release of November 6, 1970, have been compared with temperatures simultaneously measured on the surface. The scanner was operated at 2000 ft altitude at 0900 and 1145, after oil release at 0840. Corresponding surface temperatures were measured at 0900 and 1200. The tabulation below shows the scanner temperature (Teq), and the temperature of the top 2 mm layer of water (T_s^w).

Aircraft Pass	Time	Teq	T_s^w	ΔT
1	0858	14.2-14.5	15.4	0.9-1.2
2	0902	13.2-13.6	15.4	1.8-2.2
3	1144	13.5-14.3	15.5	1.2-2.0

Between passes 1 and 2, T_s^w was constant, Teq varied by 1 C, the instrument reference temperature varied by 2.5 C and there were apparent power supply problems. Passes 1 and 2 can be used only as indicators of relative temperatures. There was no difficulty in calibration of pass 3, so its ΔT value should be attributable to water emissivity value, reflection of sky radiance, absorption and emission in the atmospheric path to the passive infrared sensor, and vertical temperature gradients near the water surface.

The surface air temperature was generally lower than T_s^w and the water temperature increased to 16.7 at 20 mm depth. This temperature gradient is caused by evaporation, and water-to-air heat conduction (McAlister, 1969). Assuming the gradient continues linear from 2 mm depth to the 20 mm infrared measurement depth, 0.15 C of the observed ΔT is explained.

The Teq value is uncertain because of poor accuracy of water emissivity and sky radiance information. Emissivities reported range from 0.970 to 0.993 (Buettner and Kern, 1965; Buettner, Kern, and Cronin, 1965; Saunders and Wilkins, 1966; Saunders, 1967; Griggs, 1968; Lee, 1969; Anding and Kauth, 1970) and caused an uncertainty in Teq greater than the observed ΔT. From the field data of Weiss (1963), Oshiver, et al. (1965), and Saunders (1967), 0.5 C of ΔT is explained by the above uncertainties.

Atmospheric radiation absorption and emission a 1.0 C error in Teq at 2000 ft altitude, as indicated by Oshiver, et al. (1965), Garnier (1971), and Marlatt and Harlan (1971).

This explains 1.0 C of ΔT. The total explained ΔT is 1.65 C, which is close to the observed value and the ΔT of 2.2 C given by the equation of Pickett (1966). It is apparent that Run 3 contains a consistent temperature data set.

OIL SLICK TEMPERATURES

In slicks of No. 4 and 6 oils, oil surface temperatues (T_s^o) were equal to T_s^w for thin films. T_s^o was up to 7.5 C higher than T_s^w for millimeter thick portions of the slicks. The greatest temperature differences were at mid-day for slicks several hours old. Subsurface open water temperatures were lower than the corresponding values under warm oil.

During the 0848 pass on November 6, 1970, T_s^o equaled T_s^w. T_s^o for thick regions was measured 80 minutes later, but still was only 0.3-0.6 C above T_s^w. Comparison of infrared and ultraviolet scanner outputs showed that the infrared did not record slick edges. The scanner temperatures for oil and water (Teq^o and Teq^w) differed by up to about 3.0 C, but differences were not consistent due to scanner calibration problems.

For the 1145 pass T_s^o ranged from 15.5 C in thin films to 23.0 C in thick oil lenses. In moderate oil thicknesses, Teq^o was less than Teq^w by 0.9-2.5 C. This difference was reversed for very thick oil.

The Teq^o - Teq^w differences can be explained in terms of the temperatures and emissivities (ϵo and ϵw) of oil and water. Buettner, et al. (1965) reported ϵo for a oil film of unknown type and thickness as 0.972, compared to $\epsilon w = 0.993$. In view of the uncertainty in ϵw, $\epsilon o = 0.972$ must be regarded as a rough estimate, and using this value with $T_s^o = T_s^w$ gives calculated differences considerably smaller than those observed. The proposed ϵo value is evidently too large, and a dependence of ϵo on oil thickness is indicated, as suggested by Chandler (1970).

The rise in T_s^w with time due to solar heating was less than for T_s^o of thick oil, because water has a lower visible light absorbance than oil. It has been suggested (Chandler, 1969; Estes and Golomb, 1970; Stewart, et al., 1970) that the thermal infrared information might correlate with slick thickness, but such correlations must be ambiguous because of surface temperature variations and uncertainty in ϵ values and in the unknown ϵo - film thickness relation.

OIL FILM THICKNESS

Thickness of films was measured on November 6, 1970, December 3, 1970, and January 21, 1971, and in later experiments which involved the NRL microwave radiometer. Stewart, et al (1970) have shown that oil spectral radiance changes with thickness are small for films greater than 0.5 mm thick and that dark oil should be at least this thickness. Thickness of dark regions were 0.1-0.8, 0.1-2.4, and 0.3-0.6 mm for numbers 2, 4, and 6 oil, respectively. These values permit a photographic estimate of the minimum volume of oil in dark areas of heavy oil spills.

DETECTION AND DISCRIMINATION OF OIL TYPES

Photographic and scanner imagery have been examined according to spectral region and observed oil type, but number 4 oil was the only type studied in all bands. Photographic sensing bands are identified here by the Kodak film - Wratten filter combination used. The term positive contrast means that oil displayed more radiance than water. Some photographs from this program are given by Munday, et al (1971).

In the near ultraviolet (0.32-0.40 μm, 2403, 2492/18A), number 2 oil showed positive contrast. Interference rings were expected, but not detected. Number 4 oil showed interference rings, sharp slick edges, large positive contrast for films thinner than 50 μm, and small negative contrast for thicker regions.

In the blue band (0.40-0.50 μm; 2403/47), No. 2 oil showed strong interference rings, and moderate positive contrast in the main body of the slick. There was little radiance variation across the slick, so thickness regions were not distinguishable. Numbers 4 and 6 oil also showed strong interference colors. Thin regions showed moderate positive contrast and thick regions moderate negative contrast.

In the green-yellow band (0.50-0.62 μm, 2403/57), numbers 4 and 6 oil showed moderately. Thick regions showed large negative contrast.

In the red-near infrared band (0.62-0.80 μm, 2424/89B), number 4 oil was barely visible and thick regions showed small negative contrast, so oil detection was not practicable.

Ordinary color (SO-397, 8442, 2448/1A), infrared color (8443, 2443/12, 15) and infrared color with haze filter (8443/1A) photography of oils was tested. Infrared color was difficult to expose properly and gave poor contrast. Ordinary color for No. 2 oil showed interference rings but did not distinguish thick and thin regions. For No. 4 and 6 oil the interference rings were seen, edges appeared light blue, thin regions appeared blue, yellow or brown, and thick regions appeared gray or black. The infrared color with haze filter gave the best image and color contrast. For number 6 oil, interference rings showed well, thin regions were pink with positive contrast, thick oil dark red. Menhaden fish oil was white on a magenta water background, thin oils were not imaged, and, as noted by Barringer (1968), intermediate thicknesses were not present.

Photography is useful for oil slick detection and discrimination, a conclusion at variance with that of Estes and Golomb (1970), who state that oil slicks do not photograph well on color film. Photographic results here agree with Lowe and Hasell (1969) and with the radiance model of Stewart, et al (1970) which predicts a change from positive to negative oil/water contrast at 0.4 µm wave length, a value close to the value 0.46 µm derived from observations in the present study. The results also agree with Catoe's (1970) statement that thin slicks are detected efficiently by UV-blue band photography.

The near ultraviolet band is best for imaging edges and thin slicks, while the green band is best for delineating thick oil regions. Number 2 oil can be distinguished from No. 4 and 6 because it does not show negative contrast in the blue and green bands. Menhaden oil can be distinguished from the fuel oils by its lack of interference colors.

Ordinary color film is a good accessory record for all oil spills. It distinguishes thick from thin oil, and helps differentiate between oil and natural slicks. Color infrared film may sometimes be needed to distinguish between oil and floating vegetation.

OIL SLICK SPREADING

Slick areas were measured with a polar planimeter on Tri-X film with a Wratten 47 filter or on color film. The slick edge was taken as the edge of the outer dark interference ring. True areas were calculated from vessel lengths in photographs. Hourly area values were used to calculate oil spreading rates, which were compared with rates predicted by the model of Fay (1969). This model predicts three phases of spreading of point oil releases on calm water. In phase three, spreading is caused by surface tension, and retarded by viscous drag of the boundary water layer.

A small spill should quickly enter phase three, whose spreading law is $r = k\ (\sigma^2 t^3/\rho^2 v)^{1/4}$, where r is the slick radius, k is a constant, σ is the surface tension spreading coefficient, t is time since release, ρ is water density and v is water kinematic viscosity. Assuming slick area is πr^2 and using the above equation,

$$A = \alpha t^{3/2}$$

where α represents a group of constants including k. Thus, log A versus lot t should have an intercept of log α and a slope of 1.5.

A vs t has been plotted on a logarithmic scale for releases on August 12, 1970, November 6, 1970, December 3, 1970, January 21, 1971, April 26, 1971, August 3, 1971, August 30, 1971, September 14, 1971. This plot is shown in Figure 24. A line of slope 1.5 has been drawn through the points. The intercept of this line, -1.072, was calculated from the average of log α values for all data points and differs by a factor of 6 from that used by Fay. However, his value involved an estimation of k without experimental verification.

The fit of the line to the data suggests that the phase three spreading law is applicable. Guinard (1971) found that a linear spreading law fit his observations, but no linear relation has appeared in experiments here. At short times after release, there is scatter in the data points because the releases actually were not point sources of oil, but were released over a 5 to 10 minute interval, and because near the start of spreading the phase two conditions stated by Fay may be more realistic than the phase three assumption.

The number 2 oil spill on January 21, 1971, was made in high wind conditions. Only one data point was obtained before the slick was broken up. Number 6 oil did not spread in a regular and monotonic manner. Much of the oil remained in fixed patches, perhaps due to the high oil viscosity. Fay's model does not treat the effect of oil viscosity, and he acknowledges (personal communication) that there is some oil viscosity limit above which his model fails. The lack of spreading of number 6 oil is a useful criterion for its remote sensing detection, particularly in the case of recent spills. Number 4 oil, spilled on November 6, 1970,

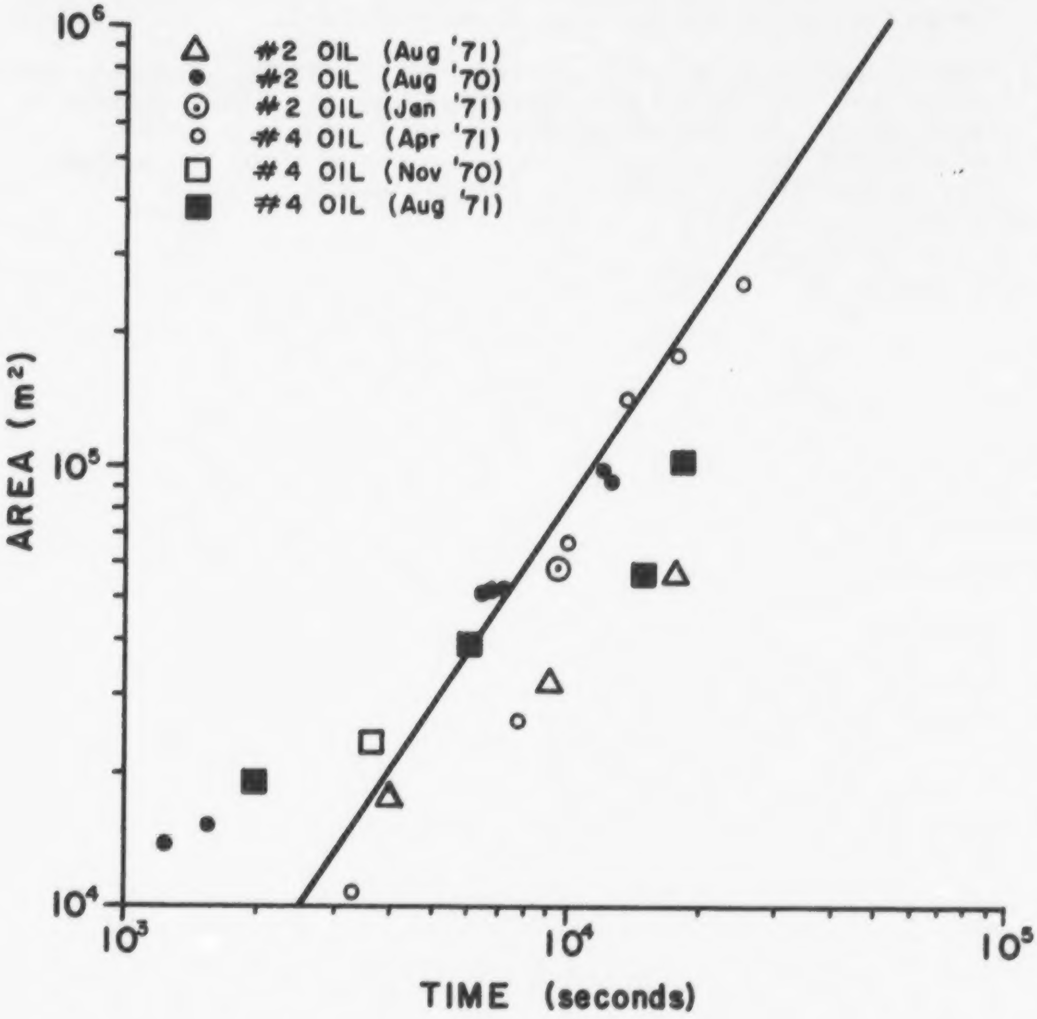

Fig. 24. Spreading rate of No. 2 and No. 4 fuel oils on sea water.

failed to spread regularly after the first hour. This lack of spreading may be caused by chemical confinement by natural surface-active organic material or by physical confinement between current convergence zones. These factors are likely to be operative in the estuarine water of the York River, where the release was made. All other number 4 and 2 oil spills spread regularly.

Other spreading models (Murray, et al, 1970; Blokker, 1964; Abbot and Hayashi, 1967; Berridge, et al, 1968) should be applied to the spreading data, but the nearly calm conditions during experiments indicated that Fay's model was most applicable to the present work.

SECTION VII

PHYTOPLANKTON IN SURFACE SLICKS AND IN ADJACENT SUBSURFACE AND NON-SLICK WATER

The surface microlayer of the ocean is being recognized as an environment which possesses certain unique chemical, physical, and biological properties. Of these, the first two have, to date, been given the most attention.

Both naturally occurring and man-made surface films have been investigated. Blanchard (1964) proposed that the surface active organic material has its source in the dissolved organic matter of the sea, and that it is transformed into particulate form and transported to the surface by bubbles. Sturdy and Fischer (1966) studied the surface tension of slick patches produced by large beds of kelp. Jarvis, Garrett, Schieman and Timmons (1967) collected samples of surface active material from different locations and found that all the material collected was similar in surface properties, indicating chemical similarities. Further study showed slick material to contain fatty esters, acids, alcohols, and hydrocarbons (Garrett, 1967a), as well as high concentrations of organic carbon, nitrogen, and phosphorous.

The need for better understanding of the biology of the surface microlayer has only recently been stated. Parker and Barsom (1970) stressed the probability that the microlayer was of considerable ecological importance because of the interaction between this layer and the air-sea interface. Ahlstrom (1969) stated that although surface films and slicks must contain communities different from those in the rest of the water column, there is little known about these organisms. David (1965) pointed out that the surface layer is of particular significance because the local environmental conditions are liable to such great and rapid changes.

Biological investigations of surface layers have been limited by problems associated with obtaining an adequate surface sample. Recently, some sampling devices have been developed which helped overcome this difficulty. Harvey (1965) originated a rotating drum sampler capable of collecting a layer of water and surface film from the upper 60 microns of sea surface. He compared samples taken by a bucket dipped to a ten centimeter depth with samples taken by his drum sampler, and found a higher concentration of organic material, including live phytoplankton, in the surface microlayer. A second type of sampling device, a screen apparatus, has been successfully used by Garrett (1965).

The present study investigates the phytoplankton found in the surface microlayer of the water column of an estuary. A Garrett-type screen collection is used to make a quantitative comparison between the phytoplankton present in this thin layer, and that found in the water one meter below. It also attempts to discover phytoplankton changes brought about by the presence of a film of slick material over the water surface.

SAMPLING PROCEDURE

Collections were made in two areas (Figure 25): the York River (I), near the Virginia Institute of Marine Science (VIMS), and, in one case, close to the Chesapeake Bay Bridge-Tunnel (II). Collection intervals were irregular because sampling was possible only in calm weather. A total of 10 sets of samples were collected on the dates shown in Table 5.

Each set of collections consisted of four samples: a pair of surface and subsurface samples in an area of water covered by a monolayer (designated a "slick" area); and a similar pair of samples in an adjacent "normal" or "non-slick" area.

One set of samples departed from this procedure. In Collection 3 a non-slick environment was sampled, then a quantity of No. 2 fuel oil was released in the area. Another set of samples (corresponding to the usual slick samples) was taken after 30 minutes.

SAMPLING DEVICES

Surface samples were taken with a screen device constructed and used according to Garrett (1965). It consisted of a 24 in. square of 16 mesh monel screen in a brass frame with upright handles and cross-bar. It is claimed that the upper 0.15 mm of surface water is sampled by this method, that sea slick material can be collected in sufficient quantity for study, and that the method is about 70 percent efficient after the first dip of the screen.

The screen was dipped into the water, withdrawn, and drained through a funnel into a wide-mouthed polyethylene jar. Ten dips were required for a sample volume of

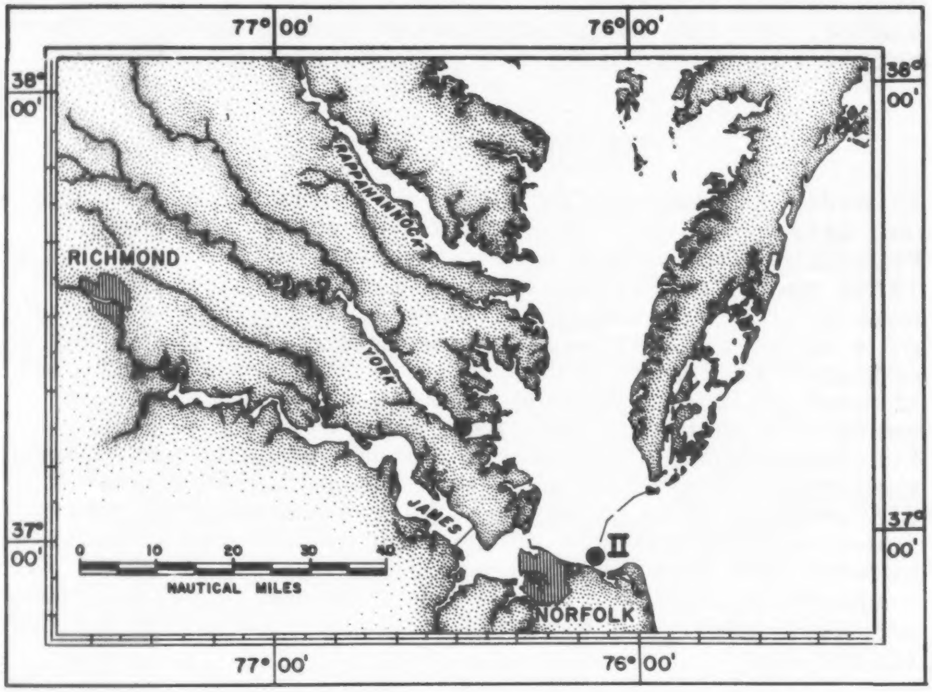
77° 00'
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Fig. 25. Plankton sample areas.

approximately one liter.

Subsurface samples were taken at a depth of one meter with a one liter Frautschy bottle.

The sampling problems presented by the irregular horizontal distribution and abundance of phytoplankton are well known (Ahlstrom, 1969; McAlice, 1970). Patchiness makes it nearly impossible to obtain an accurate representation of the phytoplankton in a given area from a single sample. Holmes and Widrig (1956) stated that in order to reduce the time required for the analysis of additional samples, the samples may be pooled and treated as one, without damaging the precision of the estimate. Sample pooling has been used in this study. In each surface collection the ten dips of the screen were combined into a single one liter sample, and for every subsurface sample three Frautschy bottle casts were made and pooled into one sample.

COMPARISON OF SAMPLERS

In order to make quantitative comparisons of surface and one meter collections, it was necessary to compare Frautschy bottle and screen sampler cell counts. A 420 liter tank was filled with filtered seawater, and a unialgal culture of the diatom *Phaeodactylum tricornutum*, of a known concentration, was added. The water was agitated to insure a homogeneous distribution of cells throughout the tank, and samples were taken at the surface with the screen, and at one meter with the Frautschy bottle. A second set of samples was taken after remixing. The experiment was later repeated with a different volume of algae. All samples were counted on the inverted microscope. There were no significant differences between the samples obtained with the two devices when the standard F, or Variance Ratio, Test was applied. Both samplers gave good estimates of the population in the tank (Table 8).

QUANTITATIVE SAMPLE TREATMENT

All field samples were stored in wide-mouthed polyethylene jars, preserved with five percent neutralized formalin, and returned to the laboratory for concentration. After three days of settling the supernatant was siphoned off, leaving a volume of approximately 500 ml. Further concentration reduced the volume to 150 ml. An additional procedure was carried out for Collection 3A (the surface slick sample taken 30 minutes after an oil spill). After

Table 8. Results of Sampler Comparison Experiments.

Exper. #	Screen Cell Counts Cells/ml	F. Btl. Cell Counts Cells/ml	Actual # Cells in Tank Cells/ml	Screen Est. Cells/ml	F. Btl. Est. Cells/ml	F Value
I	2,014	1,912	2,000	1,847	1,857	$\frac{81,579}{67,659}$ = 1.206 N.S.
	1,862	1,970				
	1,475	1,446				
	2,038	2,102				
II	1,593	2,372	2,000	1,565	2,187	$\frac{25,725}{17,487}$ = 1.471 N.S.
	1,421	2,102				
	1,681	2,087				
III	10,010	12,871	10,000	11,296	12,488	$\frac{197,187,700}{136,274,535}$ = 1.447 N.S.
	12,118	13,661				
	11,760	10,932				

settling, the No. 2 fuel oil formed a layer at the top of the sample jar. A portion of the oil was pipetted off and examined separately from the rest of the sample.

Phytoplankton cells were enumerated quantitatively by the Utermohl method, which the National Academy of Sciences (Ahlstrom, 1969) called "probably the best method known" for this purpose.

A detailed treatment of the statistical procedures involved in the Utermohl method is found in Lund, Kipling and Le Cren (1958). Assuming a random distribution of cells, the counting and sampling errors can be estimated. The Chi Square (X^2) test for randomness was applied to ten sets of five replicate counts each. Since none of these had a significant X^2 value (Table 9) the hypothesis of random distribution was supported. An estimate of the variation due to subsampling was made by counting five subsamples from each of five different samples. Confidence limits at the 95 percent level were ±3.7, ±3.3, ±2.5, ±4.8, ±3.6 percent (Table 10). The personal counting error was determined by ten replicate counts of a single subsample (Table 11), and the confidence interval at the 95 percent level was ±2.9 percent. Since this variation was within the range expected from a series of random samples, this source of error was insignificant.

For every concentrated field sample three one ml subsamples were counted. Each subsample was pipetted into a cylindrical chamber with an inside diameter of 25 mm, and allowed to settle overnight. Counts were made of a 100 mm^2 section of each chamber. The median number of phytoplankton cells per ml of water sample was calculated by the formula:

$$N = X(\frac{nc}{s})$$

where N = number of organisms per ml of original water samples
n = median number of organisms from the three counts
c = volume of the concentrate in ml
s = original volume of sample before concentration
$X = \frac{\text{area of bottom of counting chamber}}{\text{area of counted portion}}$

Ricker (1937) gave a formula for calculating the confidence intervals of a count, and Lund, et al (1958) stated that if the organisms have been shown to be randomly distributed, the confidence limits can be used to compare counts. There is a significant difference between two counts if their

Table 9. X^2 Test for Random Distribution.

	I	II	III	IV	V	VI	VII	VIII	IX	X
1.	163	1130	982	345	1328	1189	1772	337	2586	1902
2.	166	1212	1002	369	1446	1198	1790	347	2398	1912
3.	173	1197	1032	378	1334	1200	1718	327	2551	1868
4.	178	1222	1028	375	1372	1155	1792	360	2546	1931
5.	167	1190	1016	357	1361	1221	1834	332	2537	1899
X^2	.86 N.S.	4.3 N.S.	1.7 N.S.	1.3 N.S.	6.5 N.S.	1.9 N.S.	5.2 N.S.	2.0 N.S.	8.3 N.S.	1.1 N.S.

Table 10. Counts of Five Replicate Subsamples from Five Samples. Figures represent cells/ml.

	A	B	C	D	E
1.	1130	1790	982	337	354
2.	1212	1718	1002	347	369
3.	1197	1792	1032	327	378
4.	1222	1834	1028	360	375
5.	1190	1732	1016	332	357
Mean	1190	1773	1012	341	367
Stand. dev.	35.89	37.63	20.45	13.13	10.70
Stand. error	16.05	21.30	9.10	5.87	4.79
Interval est.	±44.55 or ± 3.7%	±59.13 or ± 3.3%	±25.26 or ± 2.02%	±16.29 or ± 4.8%	±13.29 or ± 3.6%

Table 11. Counts of Ten Replicate Subsamples from One Sample. Figures represent cells/ml.

1.	770
2.	763
3.	812
4.	798
5.	733
6.	801
7.	774
8.	807
9.	746
10.	724
Mean	773
Stand. dev.	31.5
Stand. error	9.9
Interval est.	±22.39 or ± 2.9%

confidence intervals do not overlap. This criterion was used to compare samples.

POPULATION STATISTICS

The phytoplankton cells in each sample were enumerated and identified, where possible, to species. The percentage composition of the samples was determined by a method recommended by Morse (1947). The first 200 cells of each sample were identified and the total number of each species divided by two to find the percentage for each species.

Diversity was calculated according to Shannon (1948):

$$H' = - \Sigma p_i \log_2 p_i$$

where H' = a proportion between the number of individuals of each species and the total number of individuals in the sample.

$p_i = n_i / N.$

n_i = number of individuals in the ith species.

N = total number of individuals in the sample.

This index is cited by Pielou (1966) as appropriate for situations, such as plankton samples, in which a collection is too large for all of its members to be counted. It is improbable that all species present in the samples were identified since the number of cells enumerated was limited to 200, but, when H' is used as a measure of diversity, the rare species have little influence on the result.

Further comparison between samples was made using Sander's (1960) dominance-affinity index. Two samples are compared by computing the percentage of the total sample represented by each species present in both samples, and summing the smaller percentage for each species. The resultant value, the index of affinity, is a measure of the percentage of organisms common to the pair of samples.

RESULTS AND DISCUSSION

Table 12 summarizes results of plankton counts. With one exception (Collection 7) all non-slick samples showed an abundance of phytoplankton that was 1.5 to 5.4 times greater than in samples from adjacent slicks. Similarly, nine of

Table 12. Results of Sample Counts, in cells/ml.

Collection #	Location	Date	Slick		Non-Slick	
			Surface	I Meter	Surface	I Meter
1	I	29 VIII 69	1561	674	2074	1312
2	II	25 IX 69	250	245	492	207
3	I	12 XII 69	284	351	544	316
4	I	22 IV 70	4700	1920	8281	1555
5	I	1 VI 70	421	1268	2257	781
6	I	28 VII 70	665	658	1000	483
7	I	28 VII 70	870	891	732	619
8	I	17 IX 70	1356	523	2202	355
9	I	17 IX 70	1686	460	3026	721
10	I	17 IX 70	62	55	131	64

ten non-slick surface samples had a greater abundance of phytoplankton than the corresponding samples from one meter--ranging from 1.2 to 6.2 times greater. The reliability of Collection 7 was doubtful because it was collected in unfavorable weather. Confidence intervals (Table 13) show that in all cases these differences were statistically significant, since their intervals never overlapped.

The cell count in the fuel oil fraction of the slick sample in Collection 3 was compared with that in the normal slick sample. It was found that the oil fraction contained a higher number of cells.

The total number of cells in each sample is divided into its component parts (Table 14) to show the percentage of the sample that is composed of diatoms, dinoflagellates, and other types of phytoplankton (including silicoflagellates and Euglenophytes). The diatoms displayed peaks of population in April and August-September. Dinoflagellates reached a population maximum in August, with a lesser increase in June. The August dinoflagellate abundance is not from the regular sampling program, but represents a surface sample taken during a dinoflagellate bloom.

Ninety-eight species were identified. Of these, 36 occurred with sufficient frequency to be considered major components of the flora. Skeletonema costatum was the dominant organism in 92.5 percent of the samples, and the second most abundant species in an additional 27.5 percent. It was totally absent from only two samples, or five percent of the total.

Comparison of diversity values for slick and non-slick areas did not show any significant trend. Comparison of values from surface and one meter samples showed that the diversity in the surface microlayer was generally lower than at one meter, as can be seen in Figures 26 and 27. Comparison of sample pairs (surface slick and non-slick; non-slick surface and one meter) by the affinity-dominance index are given in Table 15. Values range from 53.5 to 100 percent. Over half of the sample pairs have affinities over 75 percent, indicating a very homogeneous flora.

Chemical analysis of two of the slicks showed that they consisted of naturally occurring slick material. It is probable that the other samples (except Collection 3) were of similar composition.

Table 13. Confidence Intervals, at the 99% Level, for Sample Counts.

Collection #	Surface		Non-Slick	
	Slick	Non-Slick	Surface	1 Meter
1	1172 - 1357	1959 - 2195	1959 - 2195	1069 - 1245
2	212 - 295	438 - 553	438 - 553	173 - 248
3	243 - 331	487 - 608	487 - 608	273 - 366
4	4526 - 4880	8049 - 8519	8049 - 8519	1456 - 1661
5	371 - 478	2137 - 2383	2137 - 2383	712 - 857
6	601 - 735	921 - 1085	921 - 1085	429 - 543
7	797 - 950	665 - 806	665 - 806	557 - 686
8	1264 - 1455	2085 - 2328	2085 - 2328	309 - 408
9	1583 - 1796	2887 - 3172	2887 - 3172	665 - 794
10	44 - 86	104 - 165	104 - 165	46 - 89

Table 14. Composition of Surface Samples, Slick and Non-slick.

Sample #	Diatoms	Dinoflagellates	Other
1A	1210	226	125
1C	1588	238	248
2A	194	56	-
2C	475	17	-
3A	275	9	-
3C	506	30	8
4A	4606	71	23
4C	8199	-	82
5A	246	139	36
5C	902	1140	214
6A	572	93	-
6C	580	420	-
7A	644	226	-
7C	681	51	-
8A	1288	68	-
8C	2203	-	-
9A	1686	-	-
9C	3026	-	-
10A	53	7	2
10C	112	14	5

A = Slick C = Non-slick

Table 15. Affinity Index Values for Paris of Samples.

Collection #	Slick/Non-Slick (Surface)	Surface/1 Meter (Non-Slick)
1	75.0%	53.5%
2	74.5%	99.0%
3	64.5%	71.5%
4	89.5%	77.0%
5	60.5%	80.5%
6	71.0%	74.0%
7	78.5%	82.5%
8	94.0%	100.0%
9	94.0%	100.0%
10	71.0%	72.5%

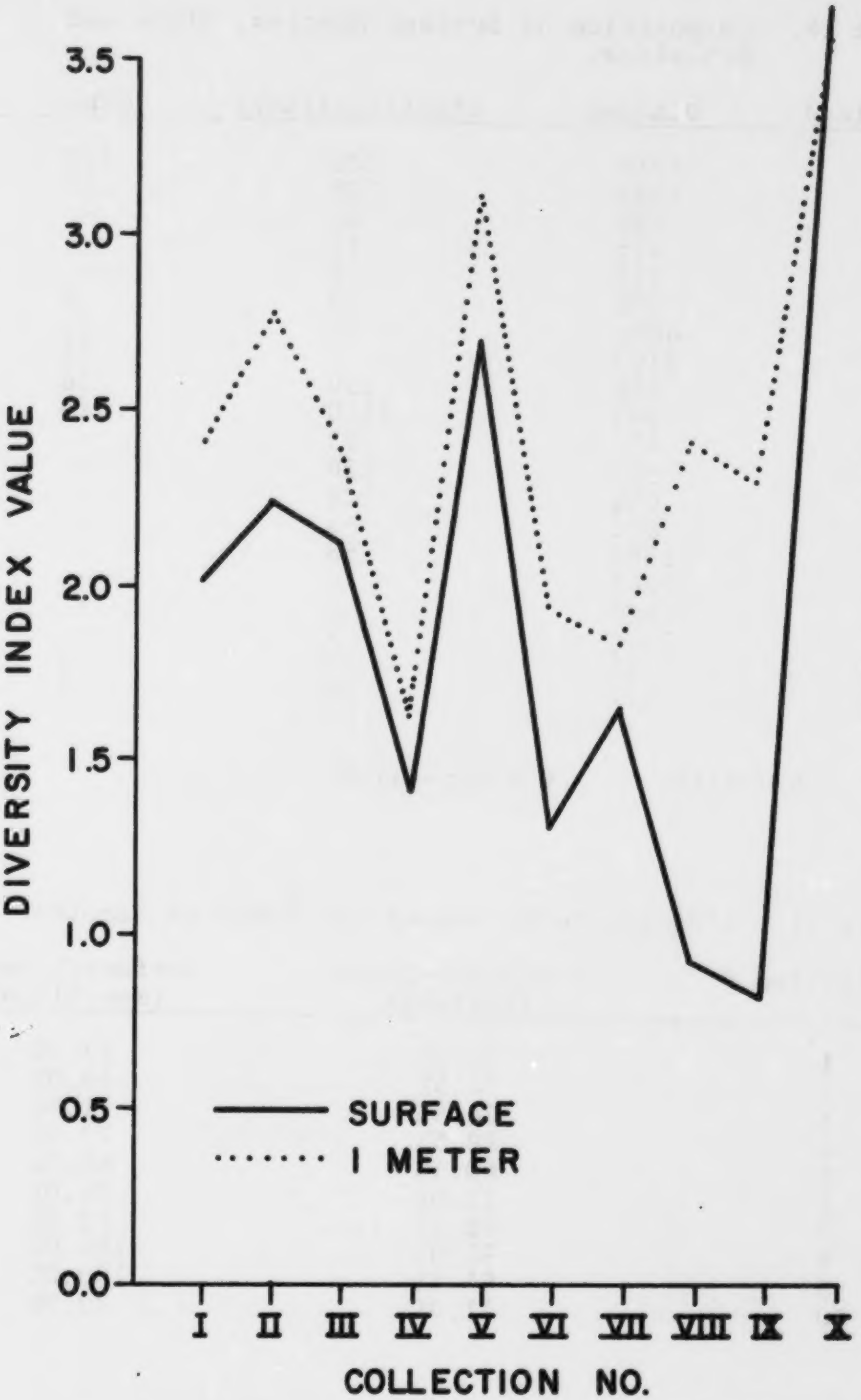

Fig. 26. Comparison of surface and one meter diversity in slick areas.

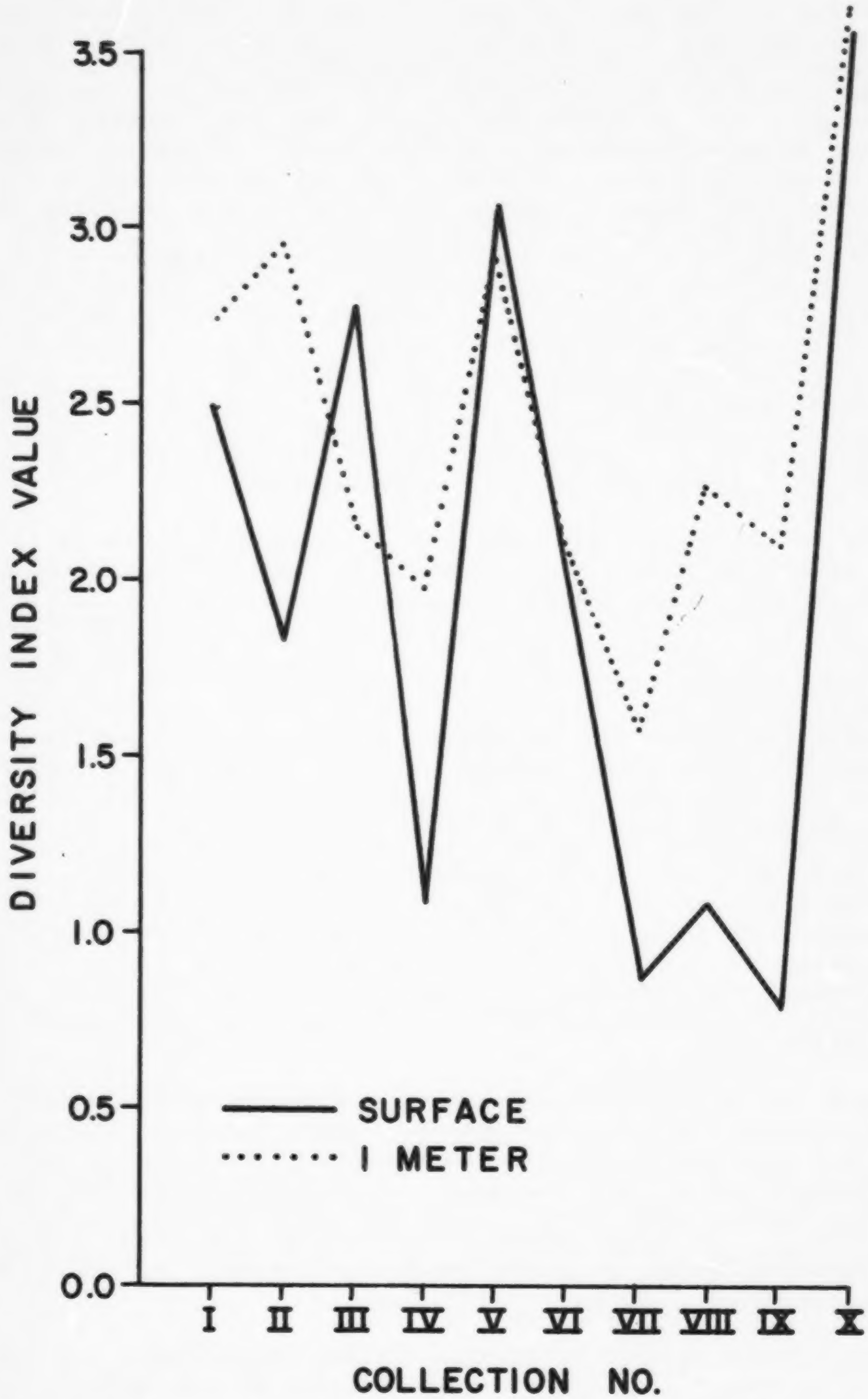

Fig. 27. Comparison of surface and one meter diversity in non-slick areas.

This study shows that, in an estuary, the surface microlayer of the water column differs substantially from the underlying subsurface water (one meter), both in the phytoplankton concentration and species diversity. The data support Harvey (1965), who reported that microlayer samples had at least four times the total number of algae and protozoans as samples from 10 cm. This information on the vertical distribution of phytoplankton should be considered when designing a phytoplankton sampling program, and is significant in studies attempting to estimate the standing crop of phytoplankton. This estimate requires accurate determination of the amount of phytoplankton in a sample, and collection of samples that are representative of the area being studied (Small, 1961). A typical "surface" sample consists predominantly of water lying at some depth beneath the actual surface layer. This extra volume of water dilutes the number of cells present and results in an underestimation of the abundance of phytoplankton per unit area of surface.

It is possible that previous estimates of primary production have erred in the same way. Depth samples for Carbon-14 measurements standardly include the surface (Steeman Nielsen, 1952a), and in some cases are restricted entirely to the surface (Doty, 1956). It remains to be shown if the cells in the surface microlayer are photosynthesizing at a maximal level. David (1965) suggested that there must be a permanent flora in the surface layer despite high light intensity, and stated two hypotheses: first, that the cells of this population would be highly specialized and able to utilize intensities that are normally thought to be inhibiting; and second, that photosynthesis would take place only when light intensity was low. There is a third possibility--that the inhibitory effect of high light intensity has been overemphasized, since most data has been obtained through laboratory studies in simulated conditions (Steeman Nielsen, 1952b, 1962; Sorokin and Krauss, 1958; Brown and Richardson, 1968).

All observations here indicate that the cells of the microlayer are healthy and active. When samples were examined live the cells appeared in good phytiological condition. Chloroplasts were abundant, and organisms capable of locomotion (dinoflagellates and some diatom species) were moving. In examination of preserved material, cells were often observed that had recently divided, or had been preparing to do so.

The lower diversity in the surface microlayer was caused by an increase in abundance of the one or two most dominant organisms (most often Skeletonema costatum, but occasionally Cerataulina bergonii or Rhizosolenia faeroense). The rare species that occurred in the one meter samples did not appear in the surface samples. This implies that certain species select the surface environment, possibly due to the light conditions.

A normal environment is assumed to support a diverse assemblage of species, while one that has been subjected to any type of pollution suffers a reduction in diversity, with an increase in numbers of individuals of the remaining species. Patrick (1949) stated that this is the first effect produced by a pollutant, and described a system which employs the distribution of species and specimens of the diatom population as an index of water pollution. This system has been successfully applied in several studies (Patrick, et al, 1954; Hohn, 1959; Patrick and Strawbridge, 1963). Wilhm and Dorris (1968) agreed that pollution results in depressed diversity, and stated that the properties of diversity indices (the fact that they are dimensionless, independent of sample size, etc) make them well suited for use as criteria for judging water quality. A study of the effect of oil pollution in a river (McCauley, 1966) found that oil produced the typical result by eliminating the plankton organisms sensitive to the toxicity, while permitting the more tolerant species to thrive.

It seems significant that there is no pattern discernible in diversity values of the four samples in each of the collections. This indicates that, although the presence of a slick does have a measurable influence on the phytoplankton in that area, it does not act in the manner usually associated with pollutants. Comparison of sample pairs by means of the affinity-dominance index supports the data obtained from diversity comparisons. In all cases the slick and non-slick pairs of samples had high affinity values, showing that their populations were very similar in composition.

Slick material might produce its effect through purely physical factors. The fact that more cells were discovered in the oil fraction of Collection 3 than in the rest of the slick sample suggests that some phytoplankton cells may have been physically entrapped in the oily layer. This would explain the absence of a reduction in diversity since the cells would, presumably, be caught at random, rather than selectively by species. Mironov and Lanskaja (1968) stated that floating organisms, such as zooplankton and phytoplankton, are particularly susceptible to injury from oil because they cannot move actively to avoid a polluted area.

There is some disagreement as to the effect of oil on the organisms of the phytoplankton, but few actual experiments have been carried out. Zobell (1964) stated that diatoms seemed to be harmed only by "prolonged exposure to large amounts of oil." In one experiment (Galtsoff, Prytherich, Smith, and Koehring, 1963) the diatom Nitzschia closterium was found to grow almost as well in medium overlayed with various kinds of oil as in the controls. However, a water-soluble extract from 25 percent crude oil was shown to retard growth of diatom cultures, and a 50 percent extract stopped growth entirely. Mironov and Lanskaja (1966) conducted experiments on 20 species of planktonic algae and showed that various oils exhibited a definite toxic effect, causing retardation in cell division and, ultimately, death.

Further investigation is necessary to determine what is causing the reduction in number of phytoplankton cells in the presence of a slick, and if there actually is a physical entrapment of the cells. Another area that requires examination is the probable correlation between the percentage of the population found in the surface microlayer on a given day, and the amount of incident radiation on that day. One would predict an inverse relationship: on a cloudy day more cells would be at the surface in order to obtain sufficient energy for phytosynthesis, especially in murky inshore waters.

SECTION VIII

CHLORINATED HYDROCARBONS IN INDIGENOUS SURFACE FILMS

Ecological and human health problems resulting from the use of chlorinated hydrocarbon pesticides and polychlorinated biphenyls make it desirable to know the role of surface films in concentrating and transporting these substances.

The distribution of chlorinated hydrocarbons between surface slick and subsurface (1 meter) water samples from the York River estuary has been evaluated and compared with data obtained by Seba and Corcoran (1969) in an attempt to establish the behavior of these compounds in a relatively unpolluted environment. Slicks were sampled by a drum skimmer (Harvey, 1965), but, as in Seba and Corcoran's work, the ratio of dissolved organics to slick organics in the sample was not measurable. Preliminary analyses of surface and subsurface samples indicated the presence of detectable concentrations of polychlorinated biphenyls (PCB) and chlorinated hydrocarbon pesticides (CHP). The similarities of chemical structure of PCB's and CHP's (especially the DDT family) caused extensive masking and interference of peaks when the samples were analyzed on the gas chromatograph. Several methods for total separation of PCB's and CHP's were tested in an attempt to obtain quantitative data on both groups. Although several researchers (Holden and Marsden, 1969, and Reynolds, 1969) have claimed success in this separation, difficulties are well known and documented (Zitko, 1971a). To date, consistent and practical total separation of PCB's and chlorinated hydrocarbon pesticides at low concentration levels (effective at 10^{-10}g/μl) has not been achieved at this laboratory. Without total separation of chlorinated hydrocarbon pesticides and PCB's, the concentration estimates for PCB's are less accurate and the concentration of some pesticides cannot be evaluated. In this work, the DDT concentration was determined by converting it to DDE by dehydrochlorination in methanolic KOH, and the PCB concentrations were estimated from uninterfered peaks in the chromatograms.

SAMPLING METHODS

Surface and subsurface samples were collected from the York River estuary at irregular intervals from November 1970 - November 1971. Slicks sampled were observed and classified as: (1) Light slick - capillary wave dampening under 0-5 mph winds, (2) medium slick - capillary wave dampening with winds estimated 5-10 mph (usually contained light debris), (3) heavy slick - capillary wave dampening with winds estimated at 10-15 mph (usually contained much debris). Non-slick surface and subsurface samples were taken for comparison of chlorinated hydrocarbon content with the different slick types. Sampling dates and locations are shown on Figure 28.

Twelve liter surface samples were taken with a boat-mounted ceramic coated drum skimmer built by NASA Wallops Island Station. This apparatus avoided contamination while sampling, and samples were taken easily and quickly. When sampling, the boat was operated in the upcurrent direction to avoid collection of engine oils. The water surface layer was picked up in a stainless steel trough and drawn under vacuum into an 18 liter glass bottle. The sampling apparatus was washed with chloroform before each day's use and flushed with new sample at each station. Only stainless steel, glass, and teflon contacted the sample; this prevented contamination of the sample by grease, oils, fats, etc, that might have high chlorinated hydrocarbon concentrations.

The subsurface samples were taken by a diver who immersed an 18 liter glass bottle to approximately 1 meter and allowed it to fill with 12 liters of water.

ANALYTICAL PROCEDURE

In the laboratory, the 12 liter sample was transferred from the sample bottle to a 20 liter glass carboy with a bottom drain stoppered with a clamped teflon tube. The sample bottle was washed three times with 250 ml of pesticide-pure petroleum ether and these washings were also added to the carboy. The carboy was stoppered and the sample and petroleum ether were shaken vigorously for 5 minutes; at the end of shaking the water layer had become cloudy. The sample was allowed to stand overnight in the carboy. The next day the clear water layer was discarded through the bottom spigot and the ether portion was collected in a 2000 ml round bottom flask. Three grams of anhydrous Na_2SO_4 was added to remove the remaining water, and the sample was redissolved and transferred to a 50 ml beaker by three 15 ml washings of pesticide pure petroleum ether. The petroleum ether was allowed to evaporate to a volume of about 0.5 ml. The 0.5 ml sample and two 1 ml ether washings of the 50 ml beaker were then added to a 3.0 ml centrifuge tube, evaporated to 0.25 ml in a jet of prepurified nitrogen, spotted on TLC plates, and developed

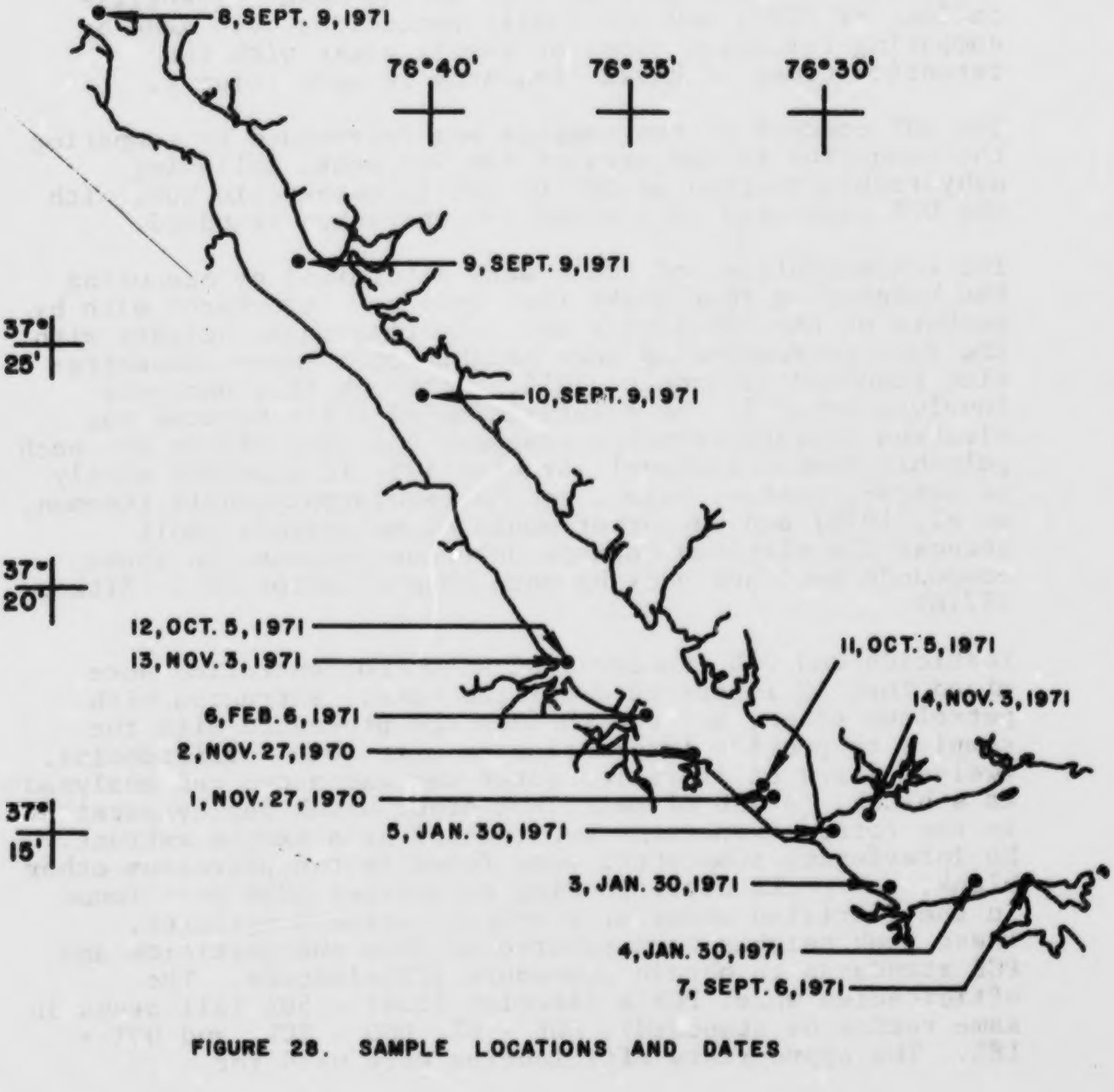
8, SEPT. 9, 1971
76°40'
76° 35'
76° 30'
9, SEPT. 9, 1971
37° 25'
10, SEPT. 9, 1971
37° 20'
12, OCT. 5, 1971
13, NOV. 3, 1971
11, OCT. 5, 1971
14, NOV. 3, 1971
6, FEB. 6, 1971
2, NOV. 27, 1970
1, NOV. 27, 1970
37° 15'
5, JAN. 30, 1971
3, JAN. 30, 1971
4, JAN. 30, 1971
7, SEPT. 6, 1971

FIGURE 28. SAMPLE LOCATIONS AND DATES

in CCl_4 to the 10 cm line in a TLC chamber according to the procedure of Breidenbach, et al (1966). Silica gel on the plate from 2 cm to 10 cm was scraped off and collected by a vacuum silica gel collection assembly. Chlorinated hydrocarbons absorbed on the silica gel were eluted into a graduated centrifuge tube by 15 ml of 50% petroleum ether-acetone solution. The samples were again reduced to 1.0 ml in a jet of prepurified nitrogen and analyzed in a Perkin-Elmer 900 gas chromatograph fitted with an electron capture detector. Two columns were used for sample analysis, one was 3% D.C. 200 on Varaport 30 80/100 mesh, the other was 5% QF-1 on Chromosorb G AW DMCS 80/100 mesh. Identifications of PCB's and DDT family pesticides were made by comparing retention times of sample peaks with the retention times of known standards on both columns.

The DDT content of the samples was determined by comparing the reduction in the area of the DDT peak, following dehydrochlorination of DDT to DDE in methanolic KOH, with the DDT peak area of a known concentration standard.

The concentrations of PCB's were determined by measuring the heights of four peaks that were not interfered with by members of the DDT family and comparing these heights with the four corresponding peak heights of a known concentration standard of Aroclor 1254. Although this analysis involves error in the quantitation of PCB's because the electron capture detector response can vary widely for each polychlorinated biphenyl, Aroclor 1254 is composed mostly of tetra-, penta-, hexa-, and heptachlorobiphenyls (Koeman, et al, 1970) and our error would be relatively small because the electron capture detector response to these compounds does not vary by more than a factor of 2 (Zitko, 1971b).

Pesticide and PCB standards of known concentration were mixed into 12 liters of distilled water, extracted with petroleum ether, and run through the procedure with the samples to provide information on extraction efficiencies. Twelve liters of distilled water was extracted and analyzed as a blank. A 750 ml petroleum ether blank was evaporated in the rotary evaporator and treated as a sample extract. No interfering substances were found in the petroleum ether blank, but peaks corresponding to Aroclor 1254 were found in the distilled water at a concentration 6 ng/liter. These peak heights were subtracted from the pesticide and PCB standards to obtain procedure efficiencies. The efficiencies were: PCB's (Aroclor 1254) - 50% (all peaks in same ratios as standard), DDE - 6%, DDD - 20%, and DDT - 18%. The appropriate efficiencies were used for determining the concentrations of PCB's and DDT in the samples.

All glassware was washed, rinsed with distilled water, dried with acetone, and rinsed with petroleum ether before each use. Samples 6 and 7 were contaminated by lubricant mistakenly applied to the rotary evaporator. Because a procedure efficiency was calculated and care was taken that each sample was treated identically, the DDT and PCB concentrations and the total chlorinated hydrocarbon count (on Table 1) represent the chlorinated hydrocarbon concentrations found in slick, non-slick, and subsurface samples.

Separations similar to Reynolds' (1969) Florisil column separation of Aroclor 1254 and CHP were tested in the laboratory and found unsatisfactory because of solvent contamination and the variability of Florisil and pesticide pure solvents. Volumes of 200 ml of hexane or 200 ml of 20% diethyl ether in hexane solution from the elution of the Florisil column in the Reynolds' procedure must be concentrated to approximately 0.5 ml in order to analyze the small amounts of chlorinated hydrocarbons obtained in this study. Gas chromatographic peaks of contaminants interferring with chlorinated hydrocarbon analysis were observed from evaporation of 200 ml pesticide standard hexane (Nanograde, Mallinckrodt) or 20% diethyl ether hexane solution to 0.5 ml. Unpredictable and incomplete elutions resulting from the variability of Florisil and the different elution properties of pesticide grade solvents (Zitko, 1971a) made the Reynolds' separation technique further undesirable for this study.

The Holden (1969) silica gel procedure for separating PCB's and CHP's uses smaller amounts of solvents, avoiding solvent purity problems, but silica gel columns, like Florisil columns, vary in their elution properties. Two types of silica gel, different column loadings, and different silica gel deactivations (by shaking with distilled H_2O for 30 minutes), were used in an attempt to separate Aroclor 1254 from DDT and DDD, but no reliable separation was found.

Thin layer chromatography procedures similar to Mulhern's (1968) for the separation and removal of organochlorine insecticides from thin layer plates were tested using Aroclor 1254 and a DDE, DDD & DDT standard, but the separations were ineffective.

Differentiation and identification of PCB's and CHP's in the samples by gas chromatography of nitrated sample extracts was not attempted because some PCB's also nitrate and clear cut identification cannot be made (Reynolds, 1969).

RESULTS AND DISCUSSION

The DDT concentrations shown in Table 16 are similar to those found in western streams by other workers (Brown and Nishioka, 1967). Duke, et al. (1970) have shown that Aroclor 1254 concentrations in water can at times be great (275 ppb) due to accidental introduction by industry, but they found values in the range of our data (100 ppt in Escambia River to non-detection in Escambia Bay) following correction of the 1254 leak.

There was an average of 16 ppt (range trace to 54 ppt) DDT o,p, and p,p' in our transitory slicks; Seba and Corcoran (1969) found 19 ppt DDT in a transitory slick in the main axis of the Florida current. The DDT content of the only semi-permanent slick sampled by this study varied from 12 ppt - 41 ppt on the two sampling dates. Seba and Corcoran found 61 ppt to 3465 ppt DDT in semi-permanent slicks associated with the mouths of drainage canals in the Biscayne Bay. They found 2-35 ppt Dieldrin and 5-34 ppt Aldrin in slick samples, but neither of these pesticides were detected here.

Corcoran (personal communication) states that PCB's occurred in very low concentrations in their samples. PCB's corresponding in retention times to Aroclor 1254 were present in our samples as indicated on Table 16.

Seba and Corcoran (1969) sampled with jars by immersing them just below the surface. Neither this method nor the drum skimmer permitted determination of the relative amounts of surface film material and water obtained in the samples. Depending on whether the slick is spread out thinly over a large area or is relatively thick but covering a small area, the chlorinated hydrocarbon concentrations in the samples could vary according to the slick area exposed to the environment. The first priorities for any future work on surface films should be the development of a field surface film thickness measuring device.

Although the data show that our classification of slick type cannot be used to determine the amount of chlorinated hydrocarbons present in the surface film, it does indicate that the concentration of total chlorinated hydrocarbons in surface films are generally higher than the subsurface concentrations. The DDT concentrations were generally

Table 16. Chlorinated Hydrocarbon Concentration Results.

Sample #	Date	Slick Type	Total Chlorinated Hydrocarbon Count*	PCB** (ppt)	DDT (ppt)	Slick Origin
1 Surface	11/27/70	1	530	51	17	Unknown
1 Subsurface	" " "	-	156	16	1	
2 Surface	11/27/70	3	640	37	54	Probably West Point Pulp Mill
2 Subsurface	" " "	-	202	17	3	
3 Surface	1/30/71	No Slick	28	2	3	
3 Subsurface	" " "		34	3	6	
4 Surface	1/30/71	3	256	21	26	American Oil Pier (recent origin)
4 Subsurface	" " "	-	264	26	5	
5 Surface	1/30/71	No Slick	338	33	3	
5 Subsurface	" " "		302	29	2	
6 Contaminated						
7 Contaminated						

Table 16. (Cont'd). Chlorinated Hydrocarbon Concentration Results.

Sample #	Date	Slick Type	Total Chlorinated Hydrocarbon Count*	PCB** (ppt)	DDT (ppt)	Slick Origin
8 Surface	9/9/71	3	178	12	Trace	Pulp Mill
8 Subsurface	" " "	-	108	8	Trace	
9 Surface	9/9/71	2	Spilled			Pulp Mill
9 Subsurface	" " "		86	7	Not Measured	
10 Surface	9/9/71	2	43	4	Trace	Unknown
10 Subsurface	" " "	-	59	5	Trace	
11 Surface	10/5/71	3	120	5	Trace	Unknown
11 Subsurface	" " "	-	58	9	Trace	
12 Surface	10/5/71	3	118	7	12	Mouth of Queen's Creek
12 Subsurface	" " "		152	11	4	
13 Surface	11/3/71	3	325	24	41	Mouth of Queen's Creek
13 Subsurface	" " "		172	12	27	

Table 16 (Cont'd). Chlorinated Hydrocarbon Concentration Results.

Sample #	Date	Slick Type	Total Chlorinated Hydrocarbon Count*	PCB** (ppt)	DDT (ppt)	Slick Origin
14 Surface	11/3/71	2	208	13	45	VIMS Ferry Pier
14 Subsurface	" " "		124	6	44	
Distilled H_2O (Blank)			66	6	Trace	

* Peak height (in graph units) of all identifiable chlorinated hydrocarbons in Chromatograms

** Peaks corresponding in retention time to Aroclor 1254.

higher in surface samples and lower in the subsurface samples; the PCB's seem to be more uniformly distributed. Possible explanations for this difference are: PCB's and DDT are likely carried in different physical states in the atmosphere, PCB's as a gas and DDT on dust particles (Harvey, 1971); PCB's and DDT enter the environment by different methods; PCB's and DDT have differing surface chemical properties. Concentration mechanism, for PCB's and CHP's in surface films and subsurface water, and the exact role the surface film has in concentrating and transporting chlorinated hydrocarbons can only be determined by extensive and expanded further studies.

SECTION IX

LIPIDS OF SURFACE FILMS ON CHESAPEAKE BAY

The objective of this work was to provide more complete information regarding lipid material in surface water and surface films. The 100 micron surface layer was sampled in the York River and Chesapeake Bay, and the samples were analysed for hydrocarbons and fatty acids by thin layer and gas-liquid chromatography.

In the past, sampling of surface water was carried out by dipping a container under the surface of the water. In Garrett's work (1965), sampling techniques were greatly refined through the use of stainless steel mesh screens that sampled the top 0.15 mm surface layer. Again using screens, Garrett (1967) took samples for chemical analysis and estimated the total lipid material to be 0.2-1.0 milligrams per liter. He tentatively identified one hydrocarbon ($C_{29}H_{52}$) and reported the existence of several fatty acids at eight stations. Garrett's work was primarily involved with the total dissolved organic material that could be extracted from seawater with chloroform. The analyses were not quantitative and comparisons between fresh and salt water were not considered.

Jarvis, et al (1967) postulated the existence of fatty esters, free fatty acids, fatty alcohols and hydrocarbons in samples taken with screens. He made no chemical analyses. From Garrett's work (1967) and from physical parameters (film pressures, surface potentials, surface viscosities, and damping coefficients) Jarvis arrived at his conclusions.

MATERIALS AND METHODS

Samples were taken along the York River and nearby areas of the Chesapeake Bay. Dates, positions and descriptions are given in Appendix 2. Some preliminary samples were taken along the Chesapeake Bay Bridge-Tunnel, but the sampling boat was unable to sample regularly due to rough sea conditions.

A rotating drum mechanism was used to take the samples. It was designed by Harvey (1965), who reported it collected larger plankton populations in surface samples in slick areas than in subsurface water. Monolayers can be taken from the water's surface and transferred to a rotating cylinder with an appropriate hydrophilic surface (Ries and Grutsch, 1968, and Ries, 1968). The drum used here was designed and built by the National Aeronautics and Space Administration's Wallops Station. It was necessary that no organic contamination be present, so all surfaces in contact with the sample had to be stainless steel and coated with Solaramic S5210-ZC (a product of the Solar Company, San Diego, California).

It is supported 3 feet off the bow of an 18 ft Thunderbird Cheyenne outboard boat by a tubular aluminum structure and a boom and winch. A stainless steel trough with a teflon blade is mounted in such a fashion as to scrape the drum as it rotates through the water, in a counterclockwise sense as viewed from the right side of the boat. The drum is normally immersed to a depth of about 4 inches in the water.

The drum is turned by an electric motor at a slightly faster rate than the boat speed, which usually requires between 8 and 10 drum revolutions per minute. Water scraped from the drum is deposited in the stainless steel trough and pumped to a sample bottle by a hand operated vacuum pump.

Slightly more than 18 liters of seawater were taken at each sampling site. Immediately upon return to the laboratory, the samples were gravity filtered through Gelman Type A glass fiber filter pads. Gravity filtration was chosen over vacuum filtration to avoid rupture of cells and release of cellular material to the filtrate. The pH of the filtrate was adjusted to 2.0-2.5 with 12N HCl to convert salts of fatty acids to the free fatty acids. At this point, 50 cc of chloroform was added to retard bacterial degradation of the sample, since it is sometimes several days before extraction can be carried out.

Next, the filtrate was placed in a continuous extraction device and bubbled through 1500 milliliters of chloroform for approximately three hours. The chloroform was then drained off and reduced in volume to about one milliliter in a vacuum rotary evaporator.

The extract was then subjected to preparative thin-layer chromatography according to Stahl (1969). This preparative thin-layer chromatography was used to "clean up" the sample and separate the various classes of compounds. Plates were coated with Silica Gel G (Merck, Darmstadt, Germany). A rapidly prepared mixture of silica gel and water was placed on 20 cm x 20 cm glass plates in a 0.25 millimeter layer by means of a spreading device (Brinkmann, Westbury, New York).

The sample spotted plate was then developed with a 90:10:1 hexane, diethyl ether, acetic acid solution. The hydrocarbon band migrated with the solvent front while the fatty acids migrated slightly less than halfway up the plate.

The bands of organic material was made visible by a 0.354 nanometer light. The hydrocarbon band was then vacuumed off the plate with a thin-layer plate vacuuming device (Brinkmann). The vacuumed silica gel was washed with methanol to remove the hydrocarbons from the relatively polar base. The methanol was evaporated to a very small volume and then extracted with hexane to remove the hydrocarbons from the methanol. This micro extraction was necessary to remove the methanol soluble calcium sulfate binder. The hydrocarbon in hexane solution was reduced to dryness by air evaporation and then redissolved in a known volume of hexane for gas chromatographic analysis.

The gas chromatographic analyses were carried out on a Perkin-Elmer Model 900 Gas Chromatograph, equipped with dual columns and flame ionization detectors, and operated under dual column compensated conditions.

For work with hydrocarbons, a 6 ft x 1/8 in. O.D. copper column was used. It was packed with a 10% SE-30 on a non-acid washed Chromosorb P (mesh 60/80) both from Applied Science, State College, Pa. A temperature program of 4 C per minute was used from 100 C to 280 C with an initial time of two minutes and final time of eight minutes. The temperature of the injectors was set at 320 C and of the manifold was set at 290 C. Helium was used as carrier gas.

The fatty acid band was also vacuumed off the plate and the silica gel washed with methanol to remove the free fatty acids which were converted to their methyl esters by the method of Metcalf and Schmitz (1961). The esters were then redissolved in a known amount of hexane and were now ready for injection in the gas chromatograph.

Fatty acid methyl esters were run with the same program as the hydrocarbons (100 C - 280 C at 4 C per minute, injector at 320 C, manifold at 290 C, initial time 2 minutes, final time 8 minutes). Glass columns (1/4 in. O.D. x 6 ft) were used to reduce any possible oxidation. The columns were packed with 5% SE-30 on Chromosorb G (AW DMCS, 80/100 mesh) prepared by Perkin-Elmer (Norwalk, Conn.).

Peaks were identified by retention time comparison with a series of standards purchased from Applied Science of State College, Pa. Areas under peaks were determined on both the standards and unknowns with the areas of each being directly proportional to their concentrations. Repeat chromatograms were made frequently on standards and blanks were also run.

RESULTS

Good separations were obtained for saturated and unsaturated mixtures of the fatty acid standards. On blank runs baseline drift was held at a minimum.

The fatty acids from 10:0 to 23:0 are reported (see Table 17). The 14:0, 16:0, 16:1, 18:0, 18:1, and 22:0 fatty acids predominate. The percentage contribution of these acids to the total free acid concentration ranged from 55 to 98% with most falling in the 70% to 90% range, as can be seen in Table 18. The amounts of fatty acid material ranged from 700 micrograms per liter to 7800 micrograms per liter. These results are very dissimilar to the results of Stauffer (1969), who investigated the fatty acids at 2 meter depths in the James River. Differences may, in part, be a consequence of high surface concentrations of lipid material. The unidentifiable material ranged from 2% to 18% with an average of less than 10%.

Normal paraffinic hydrocarbons from C_{10} to C_{24} are listed in Table 19. No concentration data was available for the first eleven samples due to difficulties with sample handling. The concentrations of the last eight samples ranged from 300 to 500 micrograms per liter. The unknown materials ranged from 20 to 45 percent with most in the 25 to 40 percent category. All the gas chromatograms of the hydrocarbon samples were rather similar to gas chromatograms of number 2 fuel oil.

The total amount of organic material collected varied from sample to sample but the variations were not related to cause in this work because fluctuations in biological communities or pollutants were not measured. The concentrations were independent of salinity. Samples were taken from the Chesapeake Bay to the Pamunkey River with salinities varying more than 20 ‰, but no geographical pattern of hydrocarbon concentrations was apparent.

A 50 Å thick slick or surface film represents about 0.005 percent by volume of a 100 micron thick water sample. Depending on the state of compression of the organic compound in the surface film, this layer should contain sufficient amounts of organics to considerably affect, by its presence or absence, the concentrations measured in the 100 micron thick sample.

Table 17. Fatty Acid Sample Concentration and Composition.

	Sample #1		Sample #2		Sample #3		Sample #4	
	µg/l	%	µg/l	%	µg/l	%	µg/l	%
10:0	-	-	-	-	-	-	-	-
11:0	011	0.14	017	0.44	-	-	-	-
12:0	104	1.32	024	0.61	010	0.24	028	1.13
13:0	147	1.87	tr	tr	-	-	148	5.92
14:0	567	7.21	248	6.31	173	4.27	148	5.92
14:1	112	1.43	-	-	-	-	-	-
15:0	207	2.64	094	2.38	091	2.25	052	2.09
16:0	2510	31.93	1503	38.21	1754	43.22	852	34.06
16:1	720	9.80	135	3.43	159	3.92	116	4.62
16:2	-	-	-	-	tr	tr	-	-
17:0	095	1.21	052	1.33	062	1.53	048	1.92
18:0	874	11.12	728	18.50	782	19.27	399	15.94
18:1	1142	14.53	628	15.95	627	15.46	379	15.16
18:2	-	-	-	-	-	-	-	-
19:0	020	0.25	050	1.27	011	0.27	013	0.52
20:0	043	0.55	013	0.33	011	0.27	028	1.13
21:0	046	0.58	033	0.83	024	0.59	013	0.52
22:0	363	4.62	052	1.33	024	0.59	205	8.19
23:0	106	1.35	011	0.27	015	0.37	009	0.35
?	742	9.44	346	8.80	314	7.73	063	2.53
Total	7861		3935		4058		2501	

Table 17. (Cont'd). Fatty Acid Sample Concentration and Composition.

	Sample #5		Sample #6		Sample #7		Sample #8	
	µg/l	%	µg/l	%	µg/l	%	µg/l	%
10:0	005	0.12	-	-	No concentrations*	-	-	-
11:0	005	0.14	-	-		-	-	-
12:0	037	0.98	004	0.16		-	030	1.11
13:0	135	3.59	051	1.92		tr	013	0.48
14:0	228	6.05	085	3.19		2.89	370	13.50
14:1	-	-	-	-		-	039	1.43
15:0	077	2.05	061	2.29		0.72	035	1.27
16:0	1316	34.96	1142	42.85		31.05	1052	38.36
16:1	274	7.29	222	8.34		1.44	314	11.44
16:2	-	-	-	-		-	-	-
17:0	061	1.62	035	1.31		1.08	018	0.64
18:0	625	16.61	407	15.29		22.74	166	6.04
18:1	603	16.03	333	12.51		31.05	383	13.98
18:2	-	-	-	-		-	-	-
19:0	017	0.46	008	0.29		-	-	-
20:0	011	0.29	030	1.14		0.36	tr	tr
21:0	013	0.35	010	0.37		-	-	-
22:0	227	6.02	101	3.80		8.66	061	2.22
23:0	015	0.41	023	0.86		-	-	-
?	113	3.01	151	5.60		-	261	9.53
Total	3764		2665				2743	

*No concentration values available.

Table 17. (Cont'd). Fatty Acid Sample Concentration and Composition.

	Sample #9		Sample #10		Sample #11		Sample #12	
	µg/l	%	µg/l	%	µg/l	%	µg/l	%
10:0	-	-	-	-	-	-	-	-
11:0	-	-	-	-	-	-	-	-
12:0	-	-	tr	tr	013	1.13	016	0.63
13:0	050	5.58	tr	tr	tr	tr	020	0.79
14:0	040	4.49	071	5.09	111	9.65	102	4.10
14:1	-	-	-	-	-	-	009	0.35
15:0	019	2.06	029	2.11	043	3.69	037	1.49
16:0	339	37.74	615	44.21	342	29.71	428	17.23
16:1	040	4.49	tr	tr	026	2.27	027	1.10
16:2	-	-	-	-	-	-	-	-
17:0	014	1.58	061	4.38	048	4.16	075	3.02
18:0	130	14.44	361	25.90	249	21.67	287	11.57
18:1	162	18.08	050	3.60	122	10.60	117	4.73
18:2	-	-	-	-	-	-	-	-
19:0	tr	tr	019	1.33	019	1.70	016	0.66
20:0	016	1.82	040	2.89	028	2.27	075	3.02
21:0	tr	tr	tr	tr	tr	tr	388	15.62
22:0	064	7.16	117	8.37	117	10.12	424	17.05
23:0	tr	tr	tr	tr	tr	tr	010	0.39
?	023	2.55	029	2.11	035	3.03	453	18.24
Total	897		1392		1151		2485	

Table 17. (Cont'd). Fatty Acid Sample Concentration and Composition.

	Sample #13		Sample #14		Sample #15		Sample #16	
	µg/l	%	µg/l	%	µg/l	%	µg/l	%
10:0	tr	tr	-	-	-	-	-	-
11:0	tr	tr	-	-	-	-	-	-
12:0	031	0.75	tr	tr	010	0.80	tr	tr
13:0	017	0.43	-	-	026	2.14	tr	tr
14:0	220	5.41	059	2.86	063	5.17	035	5.29
14:1	tr	tr	tr	tr	015	1.25	005	0.74
15:0	083	2.04	028	1.38	017	1.43	011	1.65
16:0	806	19.83	311	15.09	183	14.97	098	14.89
16:1	tr	tr	069	3.33	028	2.32	014	2.15
16:2	-	-	-	-	-	-	-	-
17:0	157	3.86	059	2.86	078	6.42	032	4.80
18:0	577	14.20	212	10.32	094	7.66	049	7.44
18:1	146	3.59	718	34.89	138	11.32	085	12.90
18:2	-	-	-	-	-	-	-	-
19:0	tr	tr	013	0.63	008	0.62	tr	tr
20:0	660	16.24	247	12.02	023	1.87	011	1.65
21:0	128	3.16	024	1.16	025	2.05	008	1.16
22:0	603	14.84	204	9.90	357	29.23	205	31.10
23:0	tr	tr	tr	tr	010	0.80	008	1.16
?	636	15.65	114	5.56	146	11.94	099	15.05
Total	4065		2058		1222		659	

Table 17. (Cont'd). Fatty Acid Sample Concentration and Composition

	Sample #17		Sample #18		Sample #19	
	µg/l	%	µg/l	%	µg/l	%
10:0	-	-	-	-	-	-
11:0	-	-	tr	tr	003	0.39
12:0	009	0.73	011	0.44	007	0.86
13:0	019	1.55	026	1.06	016	1.91
14:0	052	4.32	063	2.56	045	5.47
14:1	-	-	014	0.57	-	-
15:0	018	1.50	033	1.33	022	2.63
16:0	179	14.97	113	4.59	126	15.22
16:1	019	1.59	342	13.87	008	0.92
16:2	-	-	-	-	-	-
17:0	042	3.50	091	3.71	050	6.06
18:0	097	8.15	209	8.48	059	7.18
18:1	129	10.79	551	22.36	061	7.38
18:2	-	-	-	-	-	-
19:0	007	0.55	013	0.53	003	0.33
20:0	028	2.32	098	3.98	016	1.91
21:0	010	0.86	044	1.77	003	0.33
22:0	386	32.23	536	21.74	282	34.12
23:0	004	0.32	011	0.44	010	1.19
?	199	16.61	309	12.55	117	14.10
Total	1197		2465		827	

Table 17. (Cont'd). Fatty Acid Sample Concentration and Composition.

	Sample #20		Sample #21		Sample #22		Sample #23	
	µg/l	%	µg/l	%	µg/l	%	µg/l	%
10:0	1	0.18	9	0.18	3	0.40	16	3.97
11:0	1	0.19	10	0.20	-	-	11	2.86
12:0	3	0.42	16	0.32	7	1.02	8	2.07
13:0	12	1.66	148	2.98	-	-	29	7.35
14:0	33	4.58	59	1.19	42	5.77	30	7.67
14:1	-	-	-	-	-	-	-	-
15:0	7	0.97	14	0.28	16	2.18	17	4.30
16:0	67	9.43	270	5.40	83	11.38	36	9.09
16:1	21	2.95	26	0.52	37	5.00	45	11.49
16:2	16	2.29	11	0.22	32	4.39	23	5.75
17:0	234	32.71	2343	47.17	57	7.76	27	6.86
18:0	14	1.99	167	3.36	52	7.06	25	6.33
18:1	242	33.76	1697	34.16	135	18.44	-	-
18:2	-	-	-	-	-	-	-	-
19:0	1	0.18	40	0.81	21	2.92	5	1.27
20:0	13	1.76	39	0.79	114	15.52	15	3.82
21:0	8	1.15	-	-	64	8.78	16	4.15
22:0	-	-	-	-	-	-	-	-
23:0	-	-	-	-	-	-	-	-
?	41	5.77	116	2.33	68	9.28	90	22.83
Total	716		4967		732		395	

Table 17. (Cont'd). Fatty Acid Sample Concentration and Composition.

	Sample #24		Sample #25		Sample #26	
	µg/l	%	µg/l	%	µg/l	%
10:0	7	0.39	-	-	tr	
11:0	4	0.25	10	3.31	3	0.41
12:0	9	0.54	4	1.21	5	0.82
13:0	21	1.19	6	2.07	6	1.04
14:0	34	1.95	45	14.69	34	5.61
14:1	-	-	-	-	-	-
15:0	18	1.01	6	2.07	12	1.97
16:0	98	5.64	69	22.56	181	29.80
16:1	39	2.24	16	5.38	41	6.75
16:2	21	1.20	18	5.77	16	2.59
17:0	511	29.27	4	1.21	-	-
18:0	30	1.70	1	0.30	93	15.37
18:1	783	44.86	45	14.79	48	7.89
18:2	-	-	-	-	-	-
19:0	16	0.94	5	1.64	9	1.45
20:0	57	3.25	19	6.39	42	6.85
21:0	tr	tr	19	6.20	14	2.28
22:0	-	-	-	-	-	-
23:0	-	-	-	-	-	-
?	96	5.49	37	12.20	104	17.08
Total	1745		305		608	

Table 17. (Cont'd). Fatty Acid Sample Concentration and Composition.

	Sample #27		Sample #28		Sample #29	
	µg/l	%	µg/l	%	µg/l	%
10:0	8	0.70	7	1.04	-	-
11:0	6	0.58	15	2.18	-	-
12:0	4	0.41	11	1.61	1	0.14
13:0	29	2.69	23	3.42	-	-
14:0	24	2.22	53	7.97	26	4.03
14:1	-	-	-	-	-	-
15:0	14	1.29	8	1.23	18	2.71
16:0	105	9.76	109	16.42	53	8.12
16:1	-	-	24	3.61	44	6.77
16:2	-	-	11	1.61	18	2.80
17:0	519	48.05	-	-	-	-
18:0	68	6.31	119	17.85	9	1.45
18:1	134	12.42	145	21.83	417	63.81
18:2	-	-	-	-	-	-
19:0	11	0.99	6	0.85	-	-
20:0	56	5.20	49	7.41	-	-
21:0	11	1.05	8	1.23	35	5.32
22:0	-	-	-	-	-	-
23:0	-	-	-	-	-	-
?	90	8.36	78	11.77	32	4.88
Total	1080		665		653	

Table 18. Percentages of Predominant Fatty Acids.

Sample	14:0	16:0	16:1	18:0	18:1	22:0	Total
1	7.21	31.93	9.80	11.12	14.53	4.62	79.21
2	6.31	38.21	3.43	18.50	15.95	1.33	83.73
3	4.27	43.22	3.92	19.27	15.46	0.59	86.73
4	5.92	34.06	4.62	15.94	15.16	8.19	83.89
5	6.05	34.96	7.29	16.61	16.03	6.02	86.96
6	3.19	42.85	8.34	15.29	12.51	3.80	85.98
7	2.89	31.05	1.44	22.74	31.05	8.66	97.83
8	13.50	38.36	11.44	6.04	13.98	2.22	85.58
9	4.49	37.74	4.49	14.44	18.08	7.16	86.40
10	5.09	44.21	tr	25.90	3.60	8.37	87.17
11	9.65	29.71	2.27	21.67	10.60	10.12	84.02
12	4.10	17.23	1.10	11.57	4.73	17.05	55.78
13	5.41	19.83	tr	14.20	2.59	14.84	57.78
14	2.86	15.09	3.33	10.32	34.89	9.90	76.39
15	5.17	14.97	2.32	7.66	11.32	29.23	70.67
16	5.29	14.89	2.15	7.44	12.90	31.10	73.77
17	4.32	14.97	1.59	8.15	10.79	32.23	72.25
18	2.56	4.59	13.87	8.48	22.36	21.74	73.60
19	5.47	5.47	15.22	0.92	7.18	7.38	70.29

Table 19. Hydrocarbon Sample Concentration and Composition.

Carbon No.	Sample #1* %	Sample #2* %	Sample #4* %	Sample #5* %
10	-	0.23	0.10	0.15
11	1.80	0.12	0.08	0.41
12	5.93	0.25	0.07	0.16
13	0.19	0.21	0.31	1.07
14	9.09	1.13	0.18	6.31
15	0.68	1.06	0.76	4.20
16	2.16	3.28	1.38	6.97
17	7.80	6.68	9.24	10.41
18	5.48	7.90	11.62	8.41
19	9.60	12.79	16.10	9.68
20		13.96	9.30	6.54
21	5.67	10.03	7.11	5.14
22	8.76	-	9.20	3.87
23	10.31	1.58	4.81	5.21
24	4.64	-	1.36	1.87
?	27.89	40.74	28.35	29.60
Total	100.00	99.96	99.97	100.00

*Samples #1 thru #11 have no concentration values available for the hydrocarbons.

Sample #3 lost due to spillage.

Table 19. (Cont'd). Hydrocarbon Sample Concentration and Composition.

Carbon No.	Sample #6* %	Sample #7* %	Sample #8* %	Sample #9* %
10	0.26	0.45	0.32	0.23
11	0.11	0.18	-	0.13
12	0.33	0.23	0.10	0.13
13	0.61	0.68	0.47	1.53
14	2.58	3.12	2.50	6.36
15	4.58	3.76	3.61	8.25
16	7.40	5.12	4.66	8.49
17	9.00	8.21	8.21	11.40
18	8.37	8.00	9.70	9.75
19	14.29	14.37	10.74	8.62
20	7.19	7.37	5.95	5.43
21	5.37	6.28	4.32	3.58
22	7.50	5.31	4.93	4.77
23	4.49	6.88	3.72	1.59
24	3.39	0.97	0.88	-
?	24.60	29.07	39.88	29.23
Total	100.00	100.00	99.99	100.00

Table 19. (Cont'd). Hydrocarbon Sample Concentration and Composition.

Carbon No.	Sample #10*	Sample #11*	Sample #12		Sample #13	
			µg/l	%	µg/l	%
10	-	-	tr	tr	004.	1.26
11	0.08	-	tr	tr	002.	0.27
12	0.06	0.20	-	-	-	-
13	0.16	0.32	-	-	-	-
14	14.30	12.40	-	-	-	-
15	36.47	26.09	001.	0.32	002.	0.55
16	21.04	15.54	011.	2.48	010.	3.41
17	6.75	5.88	028.	6.27	017.	5.71
18	1.61	2.58	056.	12.53	029.	10.16
19	-	2.41	017.	3.68	019.	6.70
20	-	1.13	019.	4.25	029.	10.22
21	-	1.61	011.	2.55	011.	3.85
22	-	1.93	046.	10.34	016.	5.49
23	-	1.29	025.	5.52	008.	2.64
24	-	-	068.	15.15	009.	3.08
?	19.52	28.62	166.	36.92	133.	46.15
Total	99.97		449.	100.00	289.	

Table 19. (Cont'd). Hydrocarbon Sample Concentration and Composition.

Carbon No.	Sample #14 µg/l	Sample #14 %	Sample #15 µg/l	Sample #15 %	Sample #16 µg/l	Sample #16 %	Sample #17 µg/l	Sample #17 %
10	tr	tr	tr	tr	-	-	tr	0.06
11	001.	0.30	tr	tr	tr	tr	tr	tr
12	-	-	-	-	-	-	001.	0.09
13	001.	0.23	002.	0.78	001.	0.09	003.	0.55
14		0.11		0.14	001.	0.18	001.	0.13
15	007.	1.73	009.	3.22	007.	1.32	004.	0.66
16	025.	5.86	018.	6.67	022.	4.11	019.	3.53
17	027.	6.50	020.	7.13	019.	3.63	048.	8.75
18	052.	17.35	044.	15.92	046.	8.77	063.	11.40
19	016.	3.83	008.	2.76	023.	4.26	037.	6.68
20	051.	17.17	031.	11.26	099.	18.73	065.	11.75
21	014.	3.31	006.	2.18	017.	3.12	023.	4.15
22	033.	7.81	034.	12.41	027.	5.16	041.	7.37
23	012.	2.85	010.	3.68	013.	2.40	011.	2.07
24	016.	3.76	027.	9.77	017.	3.12	020.	3.69
?	166.	39.18	067.	24.07	239.	45.09	216.	39.14
Total	423.		276.		529.		552.	

Table 19. (Cont'd). Hydrocarbon Sample Concentration and Composition.

Carbon	Sample #18		Sample #19		Sample #20		Sample #21	
No.	µg/l	%	µg/l	%	µg/l	%	µg/l	%
10	-	-	tr	0.03	-	-	-	-
11	-	-	tr	tr	-	-	-	-
12	-	-	tr	0.04	-	-	-	-
13	tr	tr	-	-	-	-	-	-
14	tr	tr	-	-	2	0.84	36	27.21
15	005.	1.19	004.	0.81	2	0.74	16	11.56
16	023.	5.14	036.	8.14	25	12.62	29	21.44
17	020.	4.54	025.	5.61	27	13.12	-	-
18	061.	13.69	052.	11.86	33	16.37	-	-
19	012.	2.70	020.	4.60	21	10.38	10	7.15
20	054.	12.06	029.	6.62	9	4.53	2	1.68
21	023.	5.11	011.	2.59	8	3.96	3	2.10
22	033.	7.38	046.	10.50	15	7.55	7	5.04
23	010.	2.27	020.	4.60	9	4.53	-	-
24	028.	6.24	059.	13.23	21	10.18	-	-
?	178.	39.69	139.	31.39	31	15.28	0.32	23.53
Total	448.		442.		202		1.36	

Table 19. (Cont'd). Hydrocarbon Sample Concentration and Composition.

Carbon No.	Sample #22		Sample #23		Sample #24		Sample #25	
	µg/l	%	µg/l	%	µg/l	%	µg/l	%
10	-	-	-	-	-	-	-	-
11	-	-	-	-	-	-	-	-
12	-	-	-	-	-	-	-	-
13	-	-	3	0.54	-	-	3	0.51
14	-	-	50	10.12	9	6.49	65	12.24
15	12	3.77	45	9.09	16	11.35	71	13.36
16	21	6.99	80	16.25	20	14.33	77	14.65
17	-	-	-	-	-	-	-	-
18	-	-	-	-	-	-	-	-
19	52	12.90	52	10.47	16	11.22	51	9.67
20	27	8.52	50	10.16	10	7.30	11	2.11
21	15	4.14	9	1.85	9	6.76	11	2.17
22	6	1.80	18	3.70	4	2.97	17	3.18
23	90	27.12	35	7.09	5	3.24	25	4.77
24	-	-	23	4.62	12	8.38	44	8.37
?	1.14	34.62	130	26.18	39	27.57	153	28.97
Total	3.32		4.95		141		528	

Table 19. (Cont'd). Hydrocarbon Sample Concentration and Composition.

Carbon	Sample #26		Sample #27		Sample #28		Sample #29	
No.	µg/l	%	µg/l	%	µg/l	%	µg/l	%
10	-	-	-	-	-	-	-	-
11	-	-	-	-	-	-	-	-
12	-	-	-	-	-	-	-	-
13	2	0.44	tr	tr	9	0.86	-	-
14	59	13.52	23	10.47	75	7.53	51	9.62
15	37	8.46	13	5.84	31	3.13	77	4.99
16	34	7.79	47	21.29	86	8.56	84	15.75
17	-	-	-	-	-	-	-	-
18	-	-	-	-	-	-	-	-
19	53	12.04	19	8.41	81	8.08	40	7.41
20	54	12.39	18	8.24	75	7.47	34	6.41
21	8	1.74	9	4.12	27	2.74	10	1.85
22	7	1.59	14	6.18	197	19.67	16	2.99
23	9	2.09	3	1.37	93	9.30	69	12.97
24	40	9.07	11	4.72	31	3.13	64	11.97
?	135	80.79	65	29.14	296	29.64	139	26.01
Total	437		222		1000		535	

Depending on the state of compression of the organic compound in the surface film, this layer should contain sufficient amounts of organics to considerably affect, by its presence or absence, the concentrations measured in the 100 micron thick sample.

In Tables 20 and 21 fatty acid and hydrocarbon concentrations are reported for samples taken in a slick, out of the slick and in the slick with a bottle dipped under the surface. The fatty acids are more concentrated in the slick samples than in non-slick samples. Just the opposite is true for the hydrocarbon samples, indicating the slick may force more hydrocarbons into solution outside and under the slick.

The fatty acid concentrations for non-slick areas and bottle samples are in the same range as reported by Slowey, Jeffrey, and Hood (1962) for the Gulf of Mexico surface waters. At this point, it seems these results do not support Garrett's claim (1967) that surface fatty acid concentrations are independent of slicks in the area.

Table 20. Fatty Acid Concentrations in Slicks and Non-Slicks.

	Slick (Skimmer) mg/l	Non-Slick (Skimmer) mg/l	Bottle (Slick) mg/l
1 (Samples 21,22,23)	4.967	0.732	3.95
2 (Samples 24,25,26)	1.745	0.305	0.608
3 (Samples 27,28,29)	1.080	0.665	0.653

Table 21. Hydrocarbon Concentrations in Slicks and Non-Slicks.

	Slick (Skimmer) mg/l	Non-Slick (Skimmer) mg/l	Bottle (Slick) mg/l
1 (Samples 21,22,23)	0.136	0.332	0.495
2 (Samples 24,25,26)	0.141	0.528	0.437
3 (Samples 27,28,29)	0.222	1.000	0.535

SECTION X

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SECTION XI

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SECTION XII

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APPENDIX

PROGRAM DESCRIPTION
FOR
OIL SLICK MOTION

The program computes current paths from input wind and tidal current data; and predicts the motion of surface water masses or oil slicks on surface water masses, in the case when the motion is due to wind and to surface tidal currents. Suitable tidal current data can be obtained from tables of the U. S. Coast and Geodetic Survey. In a single run, current paths can be computed for any number of sets of input data. The program is processed by an IBM 1130 computer.

The program first reads housekeeping data and labels the printer output page. Then, tidal current data from up to ten stations are read, consisting of station latitude and longitude, times of slacks and maximum currents, and current velocities. Finally, the initial location of interest, a start and stop time, wind factor, and wind velocity versus time are read as input.

The bulk of computation takes place in a cycle within a loop, in which each pass of the cycle accounts for a single station. For each station, the phase of the tidal cycle is determined by comparing the time of interest with the times of slack waters, maximum flood, and maximum ebb. The current magnitude between maxima is calculated by inserting the phase in a sine wave and multiplying by the appropriate current maximum. The resulting magnitude is weighted by the inverse square of the distance between the station and the location of interest. Orthogonal components (weighted) of current velocity are formed from the product of this magnitude and the sine or cosine of the appropriate input-current direction.

Orthogonal (weighted) components are computed and summed only for stations as close as 5 nautical miles to the location of interest. The sums are divided by the sum of weights. To these sums are added wind velocity components multiplied by the wind factor. The resulting sums are multiplied by a time increment. The distance components are algebraically added to the coordinates of the initial location to produce a new location, and the time increment is added to the initial (start) time to produce a new time. The new time and new coordinates are printed and control returns to the beginning of the Do-loop to allow repetition of all computations using the new location and time. Repetition ceases when a stop time is reached.

If allowed by an input control number, control returns to nearly the beginning of the program in order that a new current path can be computed based on a new set of input data.

INPUT DATA

A. Card, Column, Format, and Description

Card	Column	Format	Description
1	1-10	2A5	D1, D2, label or title to be specified by user. A blank card is permissible.
2	1-4	I4	K, number of tidal current data stations per data set. The number must be right-adjusted in the field. The number of stations allowed is limited only by the input format I4.
3	1-4		KK, number of sets of data to be processed, equal to the number of current paths to be computed, where each current path requires a data set. The number of data sets allowed is limited only by the input format I4. The number must be right-adjusted.
A		12F6.0	((A (I, J), I = 1, 12), J = 1, K), tidal current data for each of the K stations. All data fields requires a decimal point.
	1-6	F6.0	A(1,J), degrees latitude of the station.
	7-12	F6.0	A(2, J), minutes (plus decimal fraction) latitude.
	13-18	F6.0	A(3, J), degrees longitude.

Card	Column	Format	Description
	19-24	F6.0	A(4, J), minutes (plus decimal fraction) longitude.
	25-30	F6.0	A(5, J), time of slack water in hours. All times must be in hours of military time (with a decimal point). The slack water may be that before either flood or ebb, where the choice is made by the user so that the input data times bracket the desired start and stop time.
	31-36	F6.0	A(6, J), time of the maximum current succeeding the slack time A(5, J), in hours military time.
	37-42	F6.0	A(7, J), magnitude of the maximum current A(6, J) in knots.
	43-48	F6.0	A(8, J), direction of the maximum current A(6, J) in degrees (toward).
	49-54	F6.0	A(9, J), time of succeeding slack water in hours military time.
	55-60	F6.0	A(10, J), time of succeeding maximum current in hours military time.
	61-66	F6.0	A(11, J), magnitude of the maximum current A(10, J) in knots.
	67-72	F6.0	A(12, J), direction of the maximum current A(10, J) in degrees (toward).
			Additional cards A as needed, controlled by K.
B		12F6.0	(B(I), I = 1, 6), initial data, and F, wind factor.
	1-6	F6.0	B(1), degrees latitude of initial location.

Card	Column	Format	Description
	7-12	F6.0	B(2), minutes (plus decimal fraction) latitude of initial location.
	13-18	F6.0	B(3), degrees longitude of initial location.
	19-24	F6.0	B(4), minutes (plus decimal fraction) longitude of initial location.
	25-30	F6.0	B(5), start time in hours military time.
	31-36	F6.0	B(6), stop time in hours military time.
	37-42	F6.0	F, wind factor, as a fraction ($F \leq 1.0$) of wind speed assumed by the moving object or water mass, over and above the movement due to tidal currents alone.
W		12F6.0	((W(I, J), I = 1, 2), J = 1, JJ), the hourly wind velocity, where JJ is the number of on-the-hour wind velocities needed to bracket the start and stop times.
	1-6	F6.0	W(1, J), wind magnitude in knots during hour $J-\frac{1}{2}$ to $J + \frac{1}{2}$.
	7-12	F6.0	W(2, J), wind direction in degrees during hour $J-\frac{1}{2}$ to $J + \frac{1}{2}$.
			Additional columns as needed for additional pairs of wind magnitude and direction, controlled by JJ.
			Cards A, B, and W are repeated as needed, controlled by KK.

B. Preparation of Input Data

Card 1: The label is included for convenience of the user. It can include the date or any code number.

Card 2: The number of tidal current data stations must be decided by the user. The decision should be based on the proximity of stations to the initial location and to estimated subsequent locations. The density of stations in the area of interest may need to be high, if the area has a detailed current structure. Stations further than 5 nautical miles from a location along the current path are neglected in the computations.

Card 3: A number of data sets may be processed to yield a current path for each set. The number is decided by the user.

Cards 4 to 3 + K: Tidal current data can be obtained from Tidal Current Tables of the Coast and Geodetic Survey, published by the U. S. Department of Commerce. Data from each station are input on a separate card. The latitude and longitude are obtained from Table 2. Slack water and maximum current times are obtained from Table 1 with time difference corrections obtained from Table 2. Magnitudes of maximum currents are obtained from Table 1 with velocity ratio corrections obtained from Table 2. Directions of currents are obtained from Table 2.

Card 4 + K: Initial location data, start and stop times, and wind factor F are decided by the user. The literature suggests that F = 0.05 is the maximum wind factor encountered in the field. The initial location must be within 5 nautical miles of (at least) one station.

Card 5 + K: The hourly wind velocity data must be supplied by the user.

OUTPUT DATA

A. Line, Column, Format, and Description

Line	Column	Format	Description
1	1-10	2A5	User label.
2, 3		A	Column headings: TIME (in) HOURS, LATITUDE (in) DEGREES (and) MINUTES, LONGITUDE (in) DEGREES (and) MINUTES.
4			Blank
D	1-6	F6.0	Time in hours military time.

Line	Column	Format	Description
	13-17	F5.0	Degrees latitude.
	27-31	F6.2	Minutes (plus decimal fraction) latitude.
	40-44	F5.0	Degrees longitude.
	54-58	F6.2	Minutes (plus decimal fraction) longitude.
			The first line D includes the start time plus the initial location. Subsequent lines D include time and current path location at quarter-hour intervals, up to the stop time.

LIMITATIONS AND VALIDATION

The following details of the program limit its applicability to a general situation:

1) The program has not been tested for extended precision.

2) Input tidal current data and the program method do not account for rotary current fields. Single directions are assumed for flood and ebb flow.

3) The program converts (forward and backward) from degrees latitude into 59.881 nautical miles, and from degrees longitude into 48.031 nautical miles. Hence, the program is presently suited (in North America) for only the Chesapeake Bay entrance. For use at other locations, the conversion factors must be changed in statements 18 + 2, 70 + 6, and 70 + 7.

4) If a computed current path moves more than 5 nautical miles away from all data stations, points of the path are determined from the last available computations in which the path was within 5 nautical miles of a data station. This peculiar feature is a result of allowing only stations within 5 nautical miles to influence the current path.

5) If the stop time exceeds the latest maximum current time of any station, computation of current components will be based on the latest maximum current velocity.

The operation was validated by 5 digit hand calculations on simulated data. The hand calculations were based on the program method as described in OUTPUT DATA, but not on the program statements themselves.

SYMBOLS DEFINITION, EXPLANATION OF CONSTANTS, AND LIBRARY ROUTINES

A. Definition of Symbols in Alphabetical Order:

A(I, J)	Tidal current data for J stations.
B(I)	Initial location data; start and stop times.
C1, C2	Longitude and latitude of a station in fractional degrees.
D1, D2	a) Label or title; b) Longitude and latitude of a point on a current path in fractional degrees.
F	Wind factor.
G1, G2	Longitude degrees and fractional minutes of a current path point.
G3, G4	Latitude degrees and fractional minutes of a current path point.
H	Current direction in radians (from north).
J	Number of time intervals, based on start and stop times, and intervals of 0.25 hours.
JJ	a) Number of hourly wind velocities needed to bracket start and stop times. b) Numbered hour for selection of wind velocity.
K	Number of tidal current data stations.
KK	Number of data sets to be processed.
KKK	Counter of data sets processed.
N	Counter of stations processed.
R	Distance between a current path point and a station.
S	Current magnitude.

T	Time in fractional hours.
TA	Stop time in fractional hours.
TB	The on-hour time preceding start time.
TT	Time in military hours.
T1, T3	First and second slack water times in fractional hours.
T2, T4	First and second maximum current times in fractional hours.
U	Sum of weighting factors, $1/R^2$.
W(I, J)	Wind velocities for J hours.
WM	Wind magnitude in knots.
WD	Wind direction in degrees.
X	Sum of north-south components of weighted surface current speed.
Y	Sum of east-west components of weighted surface current speed.

B. Explanation of Constants in Order of Appearance:

48.031	Nautical miles per degree longitude.
59.881	Nautical miles per degree latitude.
1.5708	$\pi/2$, radians per 90 degrees.
0.0174533	$\pi/180$, radians per degree.
3.14159	π , radians per 180 degrees.
239.524	59.881 times 4, where 4 results from a numerator factor of 1/4 hour.
192.124	48.031 times 4, where 4 results from a numerator factor of 1/4 hour.

Program Listing

```
*IOCS(CARD,KEYBOARD,TYPEWRITER,1132 PRINTER)
*LIST SOURCE PROGRAM
*ONE WORD INTEGERS
      DIMENSION A(12,10),B(6),W(2,10)
      KKK=0
      WRITE(3,4)
      READ(2,2)D1,D2
      WRITE(3,3)D1,D2
      READ(2,6)K
    7 READ(2,6)KK
    8 WRITE(3,5)
      READ(2,10) ((A(I,J),I=1,12),J=1,K)
      READ(2,10)B,F
      T=IFIX(B(5)/100.)
      T=T+(B(5)-T*100.)/60.
      TB=IFIX(T)
      TA=IFIX(B(6)/100.)
      TA=TA+(B(6)-TA*100.)/60.
      JJ=TA-TB+1.5
      READ(2,10)((W(I,J),I=1,2),J=1,JJ)
      WRITE(3,11) B(5),B(1),B(2),B(3),B(4)
      J=4.*(TA=T)+1
      DO 80 I=1,J
      U=0.
      X=0.
      Y=0.
      N=0.
   15 N=N+1
      IF(N-K)16,16,70
   16 IF (I-1)17,17,18
   17 D1=B(1)+B(2)/60.
      D2=B(3)+B(4)/60.
   18 C1=A(1,N)+A(2,N)/60.
      C2=A(3,N)+A(4,N)/60.
      R=((D2-C2)*48.031)**2+((D1-C1)*59.881)**2
      R=SQRT(R)
      IF (R) 19,19,21
   19 R=0.01
   21 IF(R-5.)20,15,15
   20 T1=IFIX(A(5,N)/100.)
      T1=T1+(A5,N)-T1*100.)/60.
      T2=IFIX(A(6,N)/100.)
      T2=T2+(A(6,N)-T2*100.)/60.
      T3=IFIX(A(9,N)/100.)
      T3=T3+(A(9,N)-T3*100.)/60.
      IF(T-T2)25,29,30
   25 S=A(7,N)*SIN(1.5708*(T-T1)/(T2-T1))/R**2
      GO TO 50
```

```
 30 T4=IFIX(A(10,N)/100.)
    T4=T4+(A(10,N)-T4*100.)/60.
    IF (T-T3)35,39,40
 35 S=A(7,N)*SIN(1.5708*(T-T3)/(T2-T3))/R**2
    GO TO 50
 39 S=0
    GO TO 55
 40 S=A(11,N)*SIN(1.5708*(T-T3)/(T4-T3))/R**2
 55 H=A(12,N)*0.0174533
    GO TO 60
 50 H=A(8,N)*0.0174533
 60 X=X-S*SIN(H)
    Y=Y+S*COS(H)
    U=U+1/R**2
    GO TO 15
 70 T=T+0.25
    TT=IFIX(T)
    TT=TT*100.+(T-TT)*60.
    JJ=T-TB+1.5
    WM=W(1,JJ)
    WD=W(2,JJ)
    D1=D1+(Y/U+F*WM*COS(WD*0.0174533+3.14159))/239.524
    D2=D2+(X/U+F*WM+SIN(WD*0.0174533))/192.124
    G1=IFIX(D1)
    G2=(D1-G1)*60.
    G3=IFIX(D2)
    G4=(D2-G3)*60.
    WRITE(3,11)TT,G1,G2,G3,G4
 80 CONTINUE
    KKK=KKK+1
    IF(KKK-KK) 82,83,83
 82 WRITE (3,4)
    GO TO 8
 83 CALL EXIT
  2 FORMAT(16A5)
  3 FORMAT(/16A5/)
  4 FORMAT(1H1)
  5 FORMAT(5H TIME,7X,8HLATITUDE,20X9HLONGITUDE/6H HOURS,
   6X,2(7HDEGREE 1S7X7HMINUTES7X)/)
  6 FORMAT(1014)
 10 FORMAT(12F6.0)
 11 FORMAT(F6.0,6X,2(F5.0,9X,F6.2,8X))
    END
```

APPENDIX B

LIPID ANALYSIS

Sampling Site Locations, Dates, and Descriptions.

Sample #1: August 18, 1970 — 0940 hrs
Long. 76°32'05" — Lat. 37°15'33"
Water temp. 28.0°C — Ambient temp. 27°C

The slick extended from the Yorktown Naval Weapons Station (N.W.S.) to about 1/2 mile northeast of the N.W.S. dock. The slick also extended to mid-channel. Light slick material, no particulate matter and no foam were noted.

Sample #2: August 18, 1970 — 1105 hrs
Long. 76°28'37" — Lat. 37°14'30"
Water temp. 28°C — Ambient temp. 27°C

The slick was in the vicinity of the Coleman Bridge, and was about 2 miles long and 40 feet wide. Little particulate material, no foam and heavy damping of capillary waves was reported. Increasing winds were experienced.

Sample #3: August 18, 1970 — 1215 hrs
Long. 76°28'37" — Lat. 37°15'29"
Water temp. 29.5°C — Ambient temp. 30°C

Due to increasing winds, this sample was taken in the Sarah's Creek area. The slick was reported as very light with some particulate material and very little foam. Sampling was discontinued due to the wind conditions.

Sample #4: August 27, 1970 — 1200 hrs
Long. 76°34'55" — Lat. 37°17'35"
Water temp. 28°C — Ambient temp. 29°C

A slick was found off Cheatham Annex. It was very large but it was light, with little foam and particulate material. The slick extended in both directions from the pier, up and down river and well out into the main channel. The winds were light.

Sample #5: August 27, 1970 — 1330 hrs
Long. 76°31'48" — Lat. 37°15'22"

The slick was located off the Naval Weapons Station in Yorktown in up and down river directions. It was light and had little foam and particulate matter.

Sample #6: August 28, 1970 1200 hrs
Long. 76°48'25" Lat. 37°31'54"
Water temp. 28.5°C Air temp. 29°C

The slick was located just south of the Pamunkey River Bridge at West Point near the Chesapeake Corporation Plant. Particulate material and some foam was noted in a heavy slick.

Sample #7: August 28, 1970 1245 hrs
Long. 76°45'10" Lat. 37°29'8"
Water temp. Ambient temp.

Down river from West Point a heavy slick with much particulate material and foam was noted.

Sample #8: August 28, 1970 1430 hrs
Long. 76°32'57" Lat. 37°16'37"
Water temp. 29°C Ambient temp. 29°C

A very large slick with much particulate material and foam. It extended up and down river for several miles with a width about 50 yds.

Sample #9: September 24, 1970 1030 hrs
Long. 76°26'39" Lat. 37°13'34"
Water temp. 27°C Ambient temp. 24°C

A slick was sampled off the Amoco (Yorktown) pier. It was light with some foam and particulate material.

Sample #10: September 24, 1970 1145 hrs
Long. 76°30'18" Lat. 37°14'30"
Water temp. 27°C Ambient temp. 24°C

This sample was taken under the Coleman Bridge. The slick was light with no foam and little particulate material.

Sample #11: September 24, 1970 1300 hrs
Long. 37°15'34" Lat. 76°32'07"
Water temp. 27°C Ambient temp. 25°C

This slick was light with some foam and little particulate material. The sample was taken in the Naval Weapons Station area.

Sample #12: May 15, 1971 0915 hrs
Long. 76°23'0" Lat. 37°14'20"
Water temp. 18°C Ambient temp. 20°C

The sample was taken in the Chesapeake Bay near the mouth of the York River. The slick was very light with no foam or particulate material.

Sample #13: May 15, 1971 — 0945 hrs
Long. 76°25' — Lat. 37°13'55"
Water temp. 18°C — Ambient temp. 20°C

Down river from the Amoco (Yorktown) Refinery a slick was noted. There was some foam but the slick was light.

Sample #14: May 15, 1971 — 1015 hrs
Long. 76°26'33" — Lat. 37°13'32"
Water temp. 18°C — Ambient temp. 21°C

A very heavy foamy slick was sampled just west of the Amoco Refinery pier. Hundreds of dead jellyfish were noted in the slick.

Sample #15: May 15, 1971 — 1050 hrs
Long. 76°29'25" — Lat. 37°14'17"
Water temp. 18°C — Ambient temp. 21°C

A slick was noted close to the Virginia Institute of Marine Science pier. Winds were increasing. There was some foam and some particulate material.

Sample #16: May 15, 1971 — 1125 hrs
Long. 76°32'20" — Lat. 37°17'
Water temp. 19°C — Ambient temp. 21°C

This slick was light but had much organic material. Winds were increasing.

Sample #17: May 15, 1971 — 1205 hrs
Long. 76°35'30" — Lat. 37°19'55"
Water temp. 19°C — Ambient temp. 21°C

Conditions are very similar to a no-slick sample due to increasing wind. A very slight dampening effect was reported. There was much organic material and little foam.

Sample #18: May 15, 1971 — 1245 hrs
Long. 76°38" — Lat. 32°21'35"
Water temp. 18°C — Ambient temp. 19°C

Conditions were the same as Sample #17.

Sample #19: May 15, 1971 1400 hrs
Long. 76°44'50" Lat. 37°29'
Water tem p. 18°C Ambient temp. 19°C

Conditions were the same as Samples #17 and #18.

APPENDIX C

EFFECTS OF AN ACCIDENTAL SPILL OF NO. 6 FUEL OIL ON A SALT MARSH

An accidental release of about 800 barrels of a No. 6 fuel oil prepared by cutting a catalytic cracking residue with a light distillate fraction occurred on or about 2000 hours on May 5, 1971, at the Yorktown, Virginia, Amoco Refinery. The oil issued from a ruptured pipeline directly into the York River and was carried by wind driven currents through the Guinea Marsh where considerable amounts of oil beached. A portion of the oil passed through channels in the marsh and moved into Mobjack Bay where it was sampled on May 6, 1971. The fraction of the spill volume confined by the marshes is unknown, but observations from vessels and a U.S.C.G. C-130 on May 6 led to an estimate of 3/4 of the total oil remaining in the marshes. The spill trajectory is shown in Figure 29. Wind and tidal current information were available near the spill point, but could not be used to justify the slick trajectory because the spill time was uncertain to ±4 hours.

From 1200 hours on May 5 to 1200 hours on May 6 the wind blew from 230°, averaging 9 knots, using hourly data taken at the Ft. Eustis, Virginia, weather station. This wind direction is in qualitative accord with the observed 50° slick direction to beaching. The tidal current influence on the oil motion may not have been great because, if the slick moved at 3.7% of the wind speed, almost exactly one tidal cycle would have been required for it to travel the 4.5 nautical miles to the beaching site.

E.P.A. investigators arrived on site on May 6, and were transported to Guinea Marsh and assisted in sampling by project personnel. An investigation to determine the effects of a No. 6 fuel oil in the marsh was commissioned by E.P.A. as a supplement and extension to planned project activities. Amoco used a dispersant, Jansolv-60, at the release point. The presence, potential toxicity, and synergistic effects of the dispersant in the marsh were studied, and a general analysis of dispersant composition was conducted.

The composition of Jansolv-60 dispersant was not disclosed upon request to the manufacturer, so analyses were conducted at this laboratory. Atmospheric pressure distillation to 128°C showed these percentages by volume.

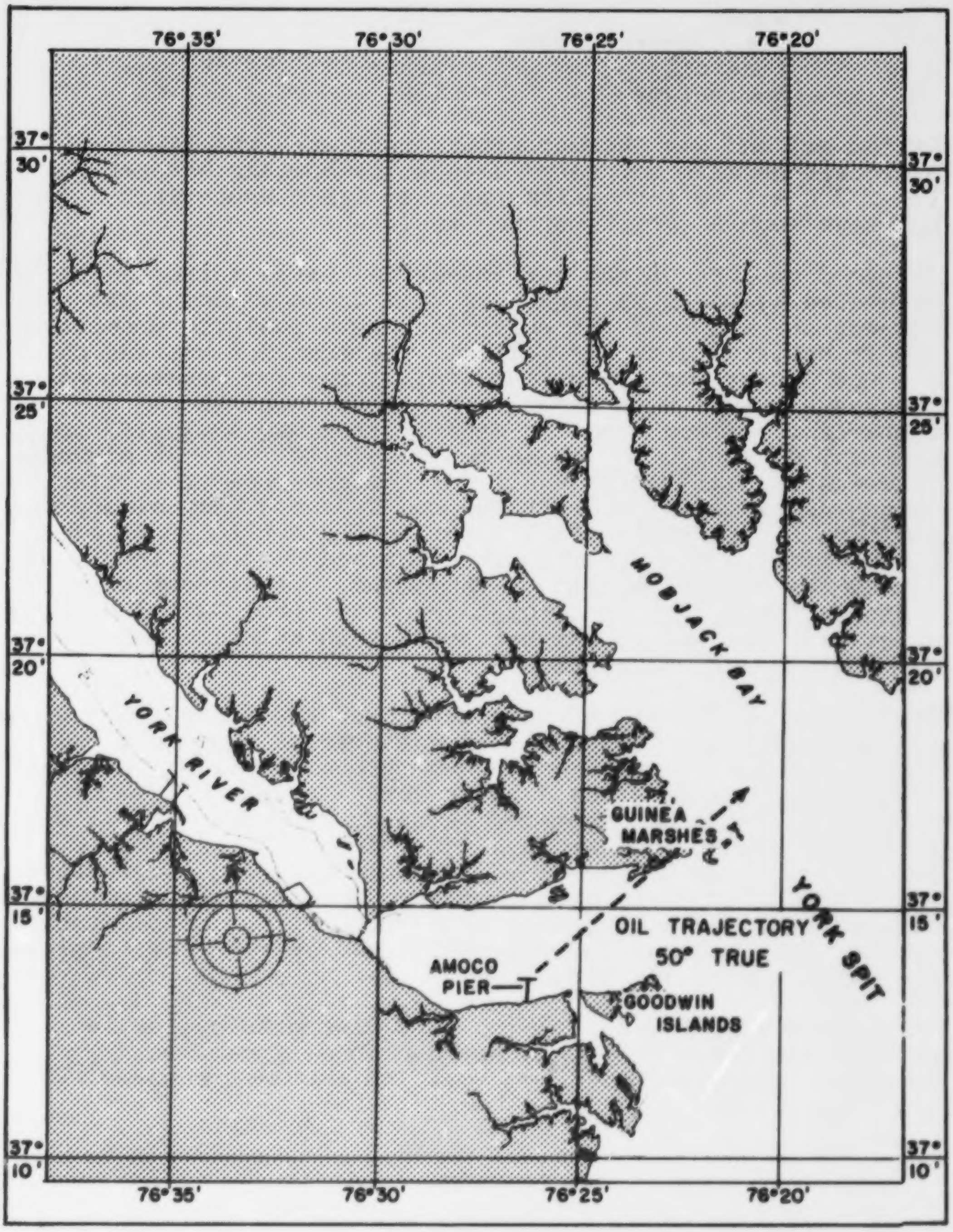
76° 35'
76° 30'
76° 25'
76° 20'
37° 30'
37° 25'
37° 20'
37° 15'
37° 10'
MOBJACK BAY
YORK RIVER
GUINEA MARSHES
YORK SPIT
OIL TRAJECTORY 50° TRUE
AMOCO PIER
GOODWIN ISLANDS

Fig. 29. Amoco oil spill trajectory.

Water	51%
Light hydrocarbons	33%
Pine oil	trace
Surfactant	16%

Silica gel and gas chromatography indicated the light hydrocarbons were saturated aliphatics boiling between 125-235°C at 760 torr which approximates a deodorized kerosene such as Jet B turbine fuel.

Infrared spectra of the surfactant indicated a predominantly saturated hydrocarbon structure with carboxyl anion groups. Aqueous solutions of the surfactant gave positive magnesium uranyl acetate tests for sodium. The ignition residue of the surfactant was strongly basic. Tests for presence of phosphate groups were negative. A portion of the surfactant residue from the distillation was subjected to Kjeldahl digestion and found to contain at least 3% nitrogen by weight. Qualitative tests for the presence of tertiary amines using the Hinsberg test, and N-bromosuccinimide were positive. A titration of 1 ml of surfactant in 20 ml of water with 0.1 N HCl, using pH electrode H^+ detection, showed the neutralization of the amine, but did not clearly indicate the proton addition to carboxyl groups at low pH. Original pH of dispersant and surfactant solution was 8.9 ± 0.1 depending on dilution.

Tests for ion charge characteristics of the dispersant (Greenberg, 1962) showed it was cationic or amphoteric. The presence of amine and carboxyl groups implies that the surfactant is a long chain amino acid. A search of commercial products uncovered Deriphat 160 (General Mills, Inc.), an amphoteric compound (disodium N-lauryl beta iminodipropionate) used as a down-hole petroleum surfactant. It is suspected that this, or a compound of similar structure, is the principal surfactant in Jansolv-60, but considerable further purification and analysis would be required to prove the exact surfactant structure.

Dispersant composition studies were discontinued, as no potentially toxic compounds or functional groups were detected that would bring to question the manufacturer's toxicity claims.

OIL SAMPLING

Samples of oil, oiled grass, and oil exposed sediment were taken for chemical analysis at the locations listed below. Location numbers and names refer to the detailed map of Guinea Marsh (Figure 30).

Date	Time	Location	Sample Description
May 6	1320	37°17'12"-76°17'30"	Slick
	1405	37°15'39"-76°20'06"	Slick
May 7	1230	37°15'36"-76°24'48"	Slick
	1240	37°15'36"-76°24'33"	Slick
	1420	1	Oil pool
May 9		1	Oiled grass
		1	Intertidal sediment
		1	Oil slick bordering marsh
		1	Oil pool at high tide time
		2	Oiled grass
		3	Snails on oiled grass
		4	Intertidal sediment core
		5	Intertidal sediment core
		6	Intertidal sediment core
		7	Intertidal sediment core
		1	Oiled peat core
		1	Intertidal sediment core
May 18		1	Oiled grass
		1	Oil covered peat
		37°13'17"-76°25'19"	Goodwin Is. Oiled grass
June 1		1	Grass and peat with entrained oil
		8	Oiled grass and mud

Samples on June 1 were at the only places where oil was visible, so samples for chemical analysis were discontinued. It is certain that oil remains absorbed in the peat and buried in sediments, but problems relating to the sampling and subsequent analysis of dispersed oil at uncertain locations made further study of a very slowly aging residual portion of the oil impractical. Beaches were surveyed completely for oil exposure on May 11, 1971. Areas with oil coverage are blackened in Figure 30. All samples were frozen in dry ice immediately upon collection and returned to the laboratory for analysis.

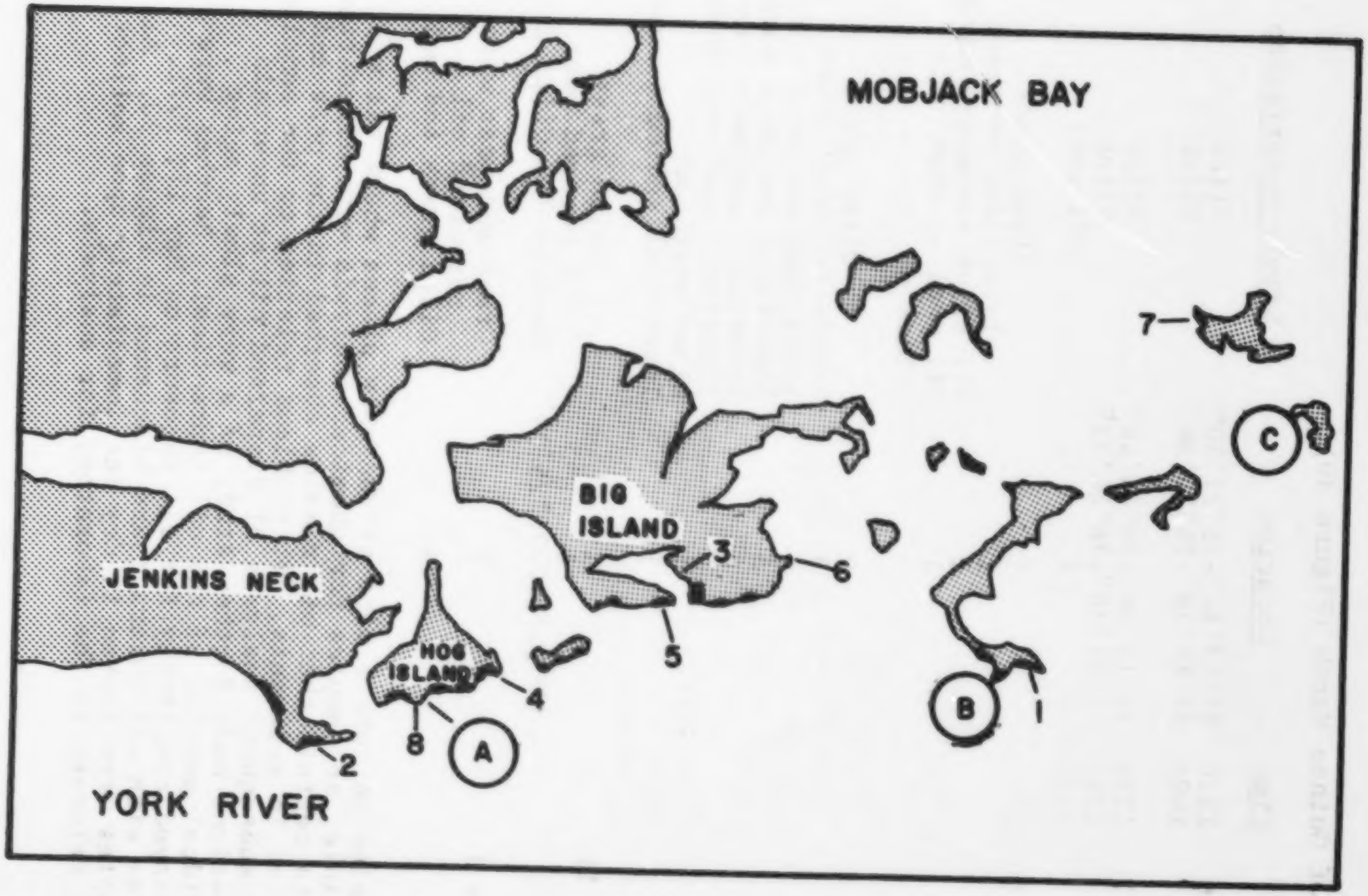
MOBJACK BAY
7
C
BIG ISLAND
3
6
5
B
1
JENKINS NECK
HOG ISLAND
4
8
A
2
YORK RIVER

Fig. 30. Guinea Marsh oil sampling locations. Black areas are oil exposed beach.

BIOLOGICAL SAMPLING

The sampling location 1 was the most heavily coated above the high tide line detected in the survey. Aerial photography from a commercial helicopter showed the most heavily oiled beaches, but did not show any oil not seen in the surface survey. A program to sample intertidal organisms near location 1 and at two areas of significantly lower oil exposure was begun on July 14-16, 1971. The biological collection stations are shown as capital letters on Figure 30. Station B is the most heavily exposed to oil, while stations A and C were free of visible oil. At each station a transect of five equally spaced substations was established in the intertidal zone. Ten cores were taken at each substation with a plexiglas corer (cores 15 cm long x 8 cm diameter).

The cores were sieved through a 1.0 mm mesh screen, and the material remaining on the screen was preserved in formalin diluted with seawater for later species identification and enumeration. Counts from individual cores were pooled and averaged for each substation for population statistics.

In December 1971, the same transects were repeated to determine the possible recovery of regions apparently adversely affected by oil.

COMPOSITION AND AGING OF THE OIL

Distillation and gas chromatographic analysis showed the oil to be a mixture of catalytic cracked crude residue and a light recycled oil. The residue consisted primarily of aromatic compounds boiling above 300°C at 1 atm, and was quite unlike residual oils from crude distillation which show obvious normal hydrocarbon peaks on gas chromatograms. The May 18 sample taken near Goodwin Island was found by gas chromatography to be a distillation residual of a paraffinic crude and not related to the Amoco spill. No Amoco oil was detected in marshes on the south bank of the York River.

A fresh sample of oil from the pipeline was provided by the Amoco Refinery. This oil was vacuum distilled and gave the boiling range composition shown in Figure 31. The lighter cuts of this oil were subjected to the F.I.A. silica gel chromatography to establish relative aromatics and saturates and portions of the aliphatic and of the aromatic efflux were collected for G.D. and G.C.-M.S. analysis.

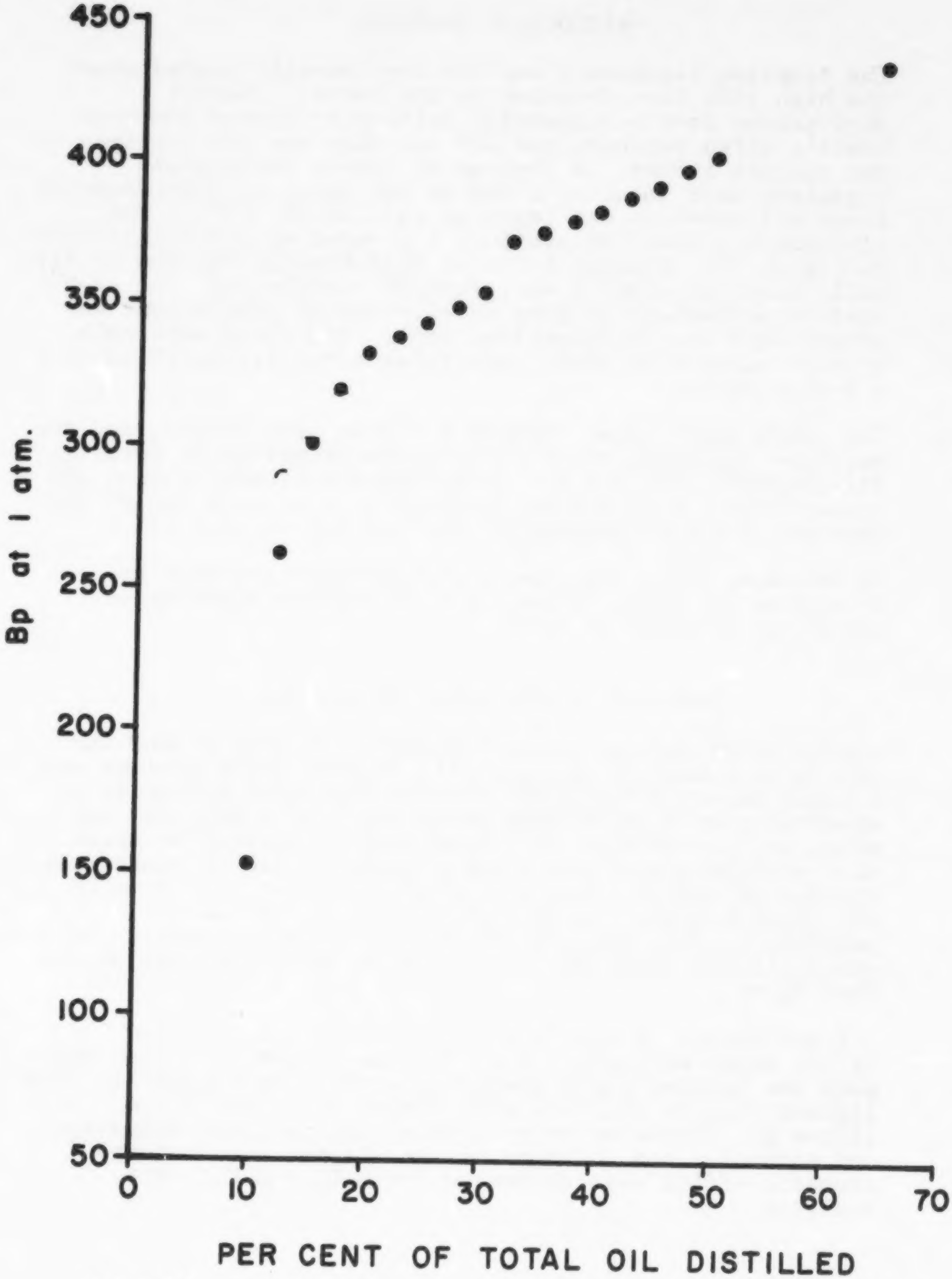

Fig. 31. Boiling range composition of Amoco spill oil.

Fraction	b.p. (°C, 1 atm)	% Aliphatic	% Aromatic
Gas Trap		83	17
1	209	8	92
2	209-221	< 1	> 99
3	221-238	0	100

A gas chromatogram of the unaged oil is shown in Figure 32. It was run on a 1/8" x 6' copper column packed with 5% SE-[illegible] on Chromosorb G AW DMCS in a Perkin-Elmer 900 Model Gas Chromatograph programmed from 100 C to 250 C at 4 C per minute. Operation was dual column compensated with F.I.D. detection. The unusual nature of this oil is indicated by the lack of easily distinguished normal hydrocarbon peaks and the bimodal distribution of peaks. Silica gel column chromatography was used to separate aliphatics from aromatics in the pentane soluble fraction of the oil. Aliphatics and aromatics were gas chromatographed separately. It was found that components boiling between 216° C and 317°C were approximately 70% aromatic with very high aromatic contents (> 90%) up to 280 C. Aromatics in this boiling range correspond to the naphthalene-anthracene range including long chain alkyl substituted benzenes and substituted naphthalenes that are not easily lost from the oil by volatilization and are low enough in molecular weight to be reasonably water soluble.

The lower molecular weight species in the first distillation cut were identified. The major components, in descending order of concentration were meta-xylene, ortho-xylene, para-xylene, ethylbenzene, and toluene. Lesser amounts of the ethyltoluene isomers, n-propylbenzene, and cumene (i-propylbenzene) were also present. These analyses were performed at NASA Langley Research Center. Samples were chromatographed through a 100 ft DPP open tubular capillary column, then introduced into a Finnegan quadrupole mass spectrometer.

The nature of the Amoco spill oil was such that little change of character could be achieved, even by lengthy aging. Pentane extracts of each of the samples listed above were analyzed by gas chromatography. By May 6, the day following the spill, the sampled oil had lost nearly all the light recycle oil, but the catalytic-cracked residue retained its original composition. Little or no further change could be noted in samples taken as late as June 1. Hence, the only observable aging of this oil spill was the rapid, immediate loss of the light recycle oil by evaporation.

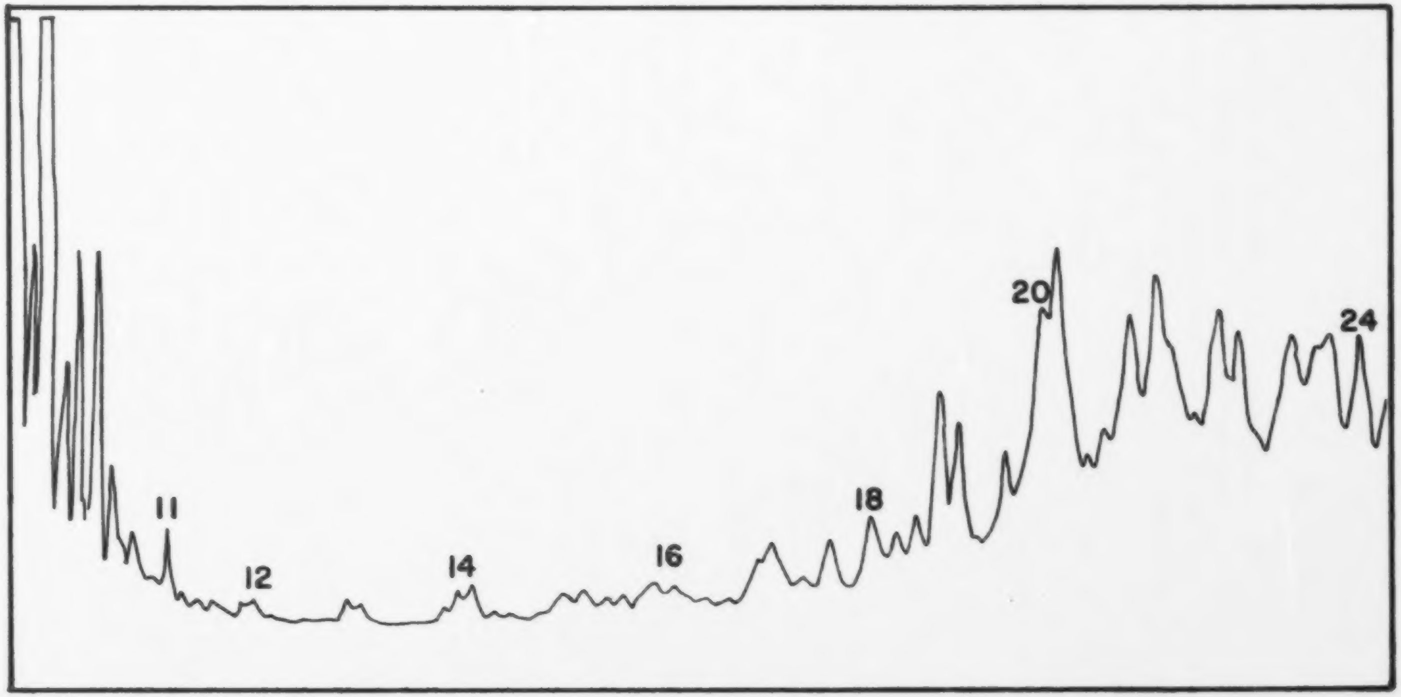

Fig. 32. Gas chromatogram of Amoco Spill Oil. Integers are carbon numbers of normal hydrocarbon peaks.

The oil had disappeared from sight by June 1, 1971, by various processes, including entrainment in the sediments, absorption into the peaty root network of the Spartina grass, and attachment to debris which was subsequently washed out of the area. Much of the residue remained in the area for the slow process of dissolution into the surrounding water.

The catalytic cracked residue appears to consist of various substituted benzenes and polynuclear aromatic species such as naphthalenes, anthracenes, etc. A program of research into the solution behavior of these aromatic species is being designed at this laboratory. However, it is probable that the alkylbenzenes present in this residue are less soluble in water, and less toxic than polynuclear aromatics of similar molecular weight. Boylan and Tripp (1971) have, for example, compiled data indicating that the naphthalenes are more toxic than the alkylbenzenes.

Gas chromatograms of the Goodwin Island oil sample showed it was a normal No. 6 fuel oil unrelated to the Amoco spill and of unknown source. Only a small area (200 ft of beach) was affected. This oil showed a bluer and less intense fluorescence of the pentane extract with 350 mm exitation than did the Amoco oil. The Amoco oil has never, to this date of reporting, lost its strong yellow-green fluorescence due to weathering. This strong fluorescence is in keeping with the highly aromatic residual character of the oil.

It should be noted that because of the highly unusual nature of the Amoco oil spill, the results of its contamination of marsh areas will not approximate that of a "normal" No. 6 fuel oil. The Amoco oil, because of its catalytic cracking treatment, does not contain a large fraction of normal paraffins, and is almost entirely aromatic.

BIOLOGICAL EFFECTS ON GUINEA MARSH

Several workers (reviewed by Cowell, 1971) have observed that heavy oil has little effect on marine grasses with rhizome systems. The predominant Guinea Marsh grass exposed to oil was Spartina alterniflora. In areas with heavy oil, leaf blades were coated and died apparently due to respiratory failure. The rhizomes survived and produced new young shoots within one month. There were no permanent kill areas and the rhizomes prevented erosion of oil exposed marsh. It is doubtful that marsh grasses would survive repeated dosing (Cowell, 1971), but recovery was prompt during the growing season.

Intertidal algae were not investigated, as there were few attached forms present above the low tide line, probably due to wave action on the sandy bottom. There were extensive Zostera beds below the low tide line, but these were not oil coated and always were at least 50 ft from the oiled shoreline.

Survival of animals exposed to the oil appeared to be the most sensitive indicators of effects, but highly motile animals which avoided the oil or fled after being affected could not be used as indicators. The intertidal macrofauna in near surface sediments were exposed to oil and unable to escape, so were sampled at the lettered locations shown on Figure 2. Intertidal sediment cores taken at stations A and B were extracted with pentane and the extracts gas chromatographed to prove the presence of oil at station B and its absence at station A. This was not done for station C because no oil beached on that island.

Organism counts at each substation were pooled for each station and the number of species (S), the number of individuals (N), and the number of individuals of the ith species (n_i) were recorded for each station for the July and December samplings.

The above count information was used to calculate:

$$\text{Species Richness} = \frac{S-1}{\ln N}$$

$$\text{Species Diversity } (H') = \frac{3.3219}{N} (N \log N - \sum_{i=1}^{s} n_i \log n_i$$

$$\text{Evenness Component } (J') = \frac{H'}{\log_2 S}$$

The Affinity Index was calculated from data at pairs of stations according to Sanders (1960). Statistical parameters for July and December are listed in Table 22.

Population indices for stations A and C are quite similar, while those for station B show great reductions in number of organisms, species, and species richness. The affinity index for stations A and C is high. The situation was nearly the same for July and December collections. It is assumed that the Amoco oil caused population reductions and

Table 22. Population Statistics of Marsh Intertidal Infauna for July (December).

		Station A	Station B	Station C
N		482 (536)	88 (107)	611 (2481)
S		32 (34)	14 (19)	34 (60)
Species Richness		5.02 (5.25)	2.90 (3.85)	5.14 (7.55)
H'		3.02 (3.21)	3.28 (3.21)	3.02 (4.03)
J'		0.605 0.631	0.861 0.756	0.594 0.684
Affinity Index	to Sta. A	-	38.7 (27.4)	62.0 (46.8)
	to Sta. B	38.7 (27.4)	-	48.2 (46.8)
	to Sta. C	62.0 (46.8)	48.2 (42.1)	-

structure alteration of the intertidal community at station B, but this is difficult to prove in the absence of a detailed survey at the stations immediately prior to the oil spill (Foster, et al., 1971). Biological collections will be repeated in May 1972 to demonstrate the recovery of station B intertidal fauna, but recovery may require several years because the oil is still present in the sediments and may exhibit the long term toxic effects of soluble aromatic compounds observed by Blumer, et al. (1970).

In conclusion, immediate effects of the oil spill on Guinea Marsh were not great. Long term effects cannot be documented as there was no baseline information to describe the previous condition of the marsh. A before and after study of a previously well sampled salt marsh which is exposed to controlled amounts of number 6 oil is being designed at this laboratory to prove long term effects. Results here, taken from similar sedimentary environments, strongly indicate a toxic effect of the Amoco oil spill. There is no present means of assessing the ultimate marsh ecosystem damage, and, were this possible, such damage could not be estimated in dollars.

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